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► **To cite this version:**

Junsoo Han, Oumaïma Gharbi. Current state of electrochemical techniques and corrosion rate analysis for next-generation materials. *Current Opinion in Electrochemistry*, 2022, 36, pp.101131. 10.1016/j.coelec.2022.101131 . hal-03776989

**HAL Id: hal-03776989**

<https://hal.sorbonne-universite.fr/hal-03776989v1>

Submitted on 14 Sep 2022

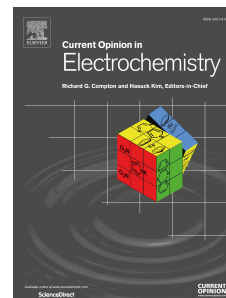
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# Journal Pre-proof

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

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PII: S2451-9103(22)00196-X

DOI: <https://doi.org/10.1016/j.coelec.2022.101131>

Reference: COELEC 101131

To appear in: *Current Opinion in Electrochemistry*

Received Date: 3 May 2022

Revised Date: 10 August 2022

Accepted Date: 31 August 2022

Please cite this article as: Han J, Gharbi O, Current state of electrochemical techniques and corrosion rate analysis for next-generation materials, *Current Opinion in Electrochemistry*, <https://doi.org/10.1016/j.coelec.2022.101131>.

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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

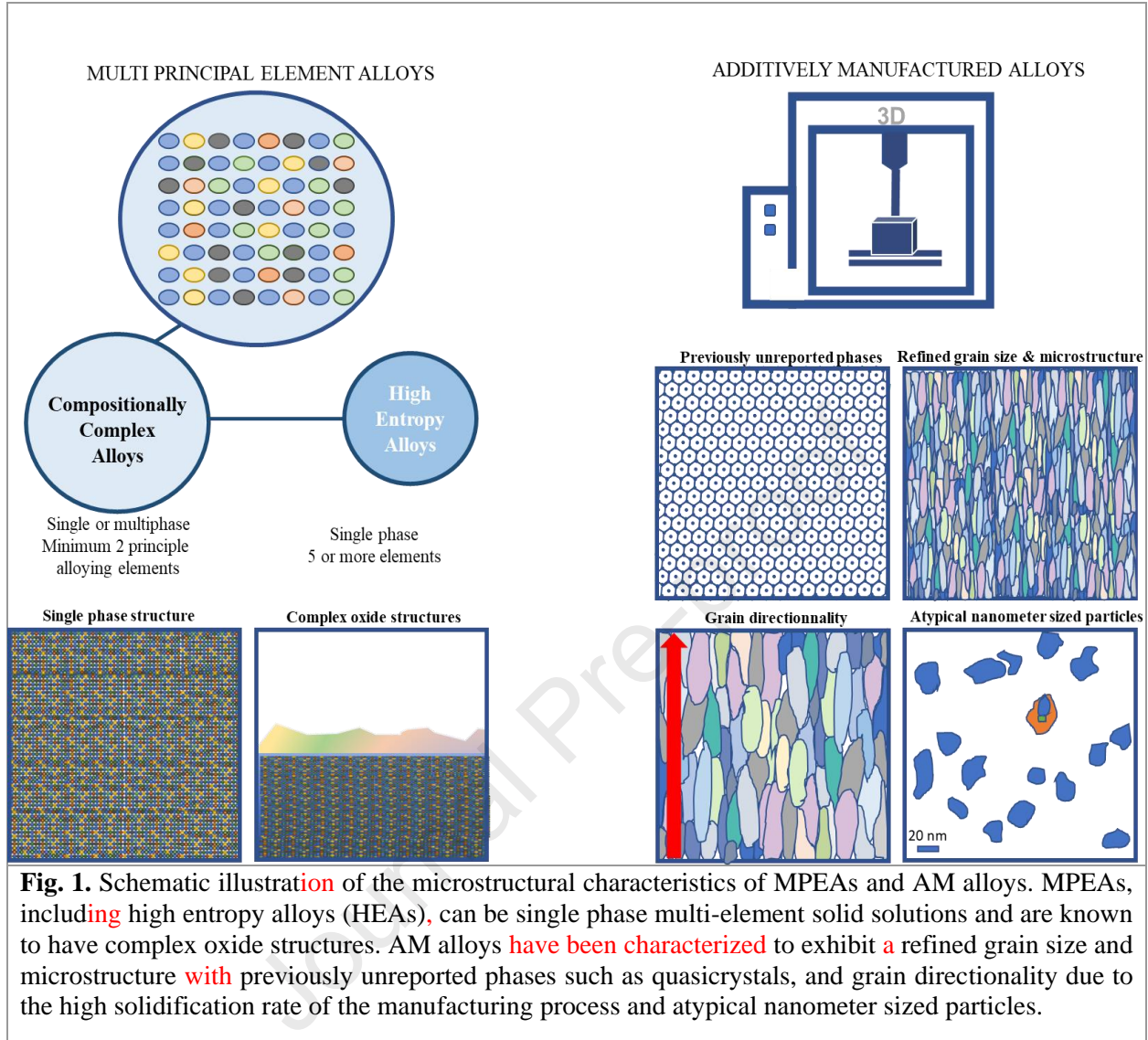
20 Since the Bronze Age, humanity has constantly developed new technological strategies and  
21 fabrication processes to produce alloys. The conventional alloy making procedure is based on adding minor  
22 alloying elements to one principal element to obtain the desired mechanical properties. In the 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) [<sup>1, 2, 3</sup>] and  
25 additively manufactured (AM) alloys described in **Fig. 1**. [<sup>4, 5</sup>].

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 [<sup>6</sup>], as well as enhanced thermal resistance and irradiation-induced corrosion  
29 [<sup>7</sup>]. 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.

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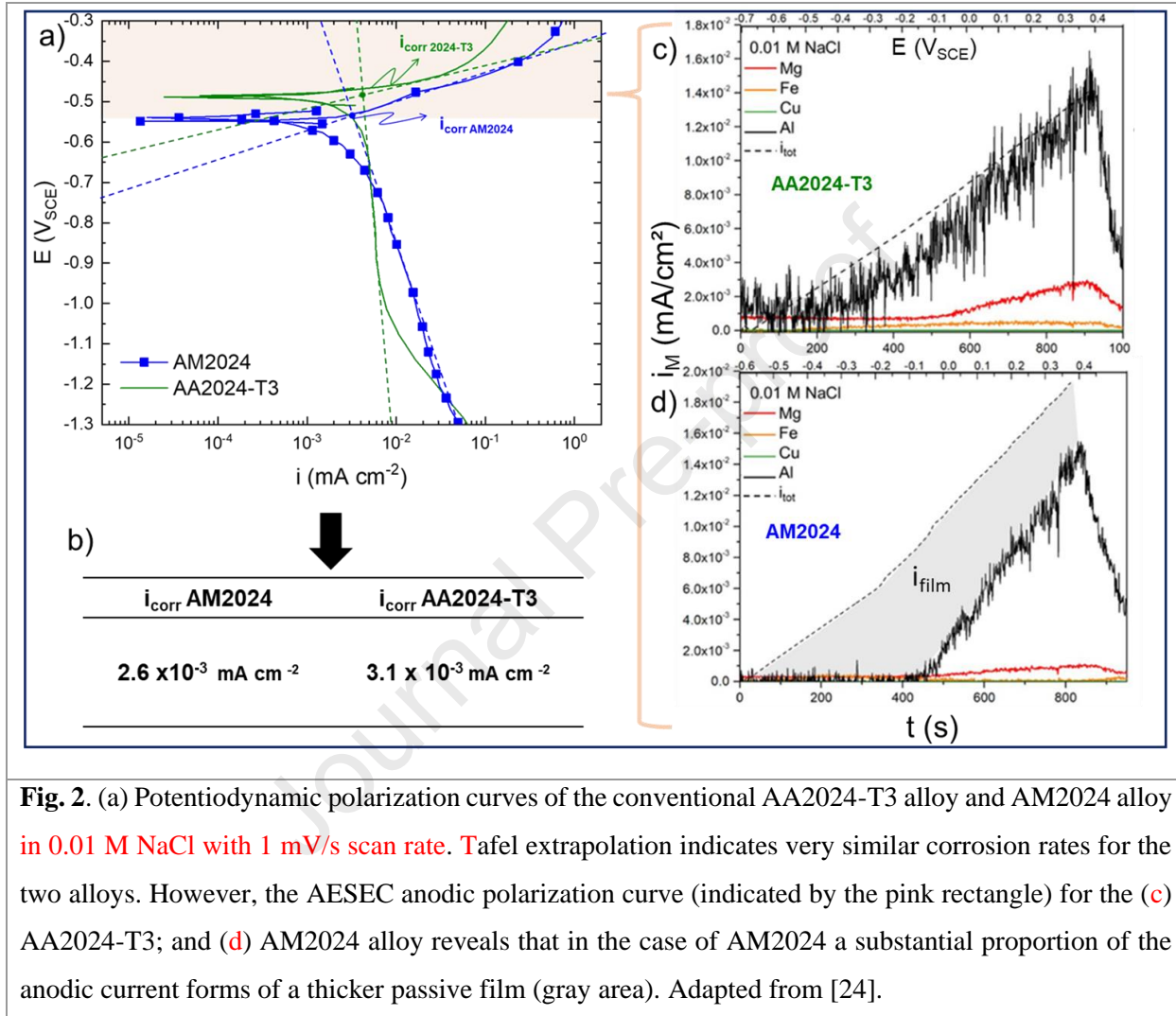
79 *Validity of corrosion rate determination: currently used techniques*

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

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 O<sub>2</sub>  
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?*

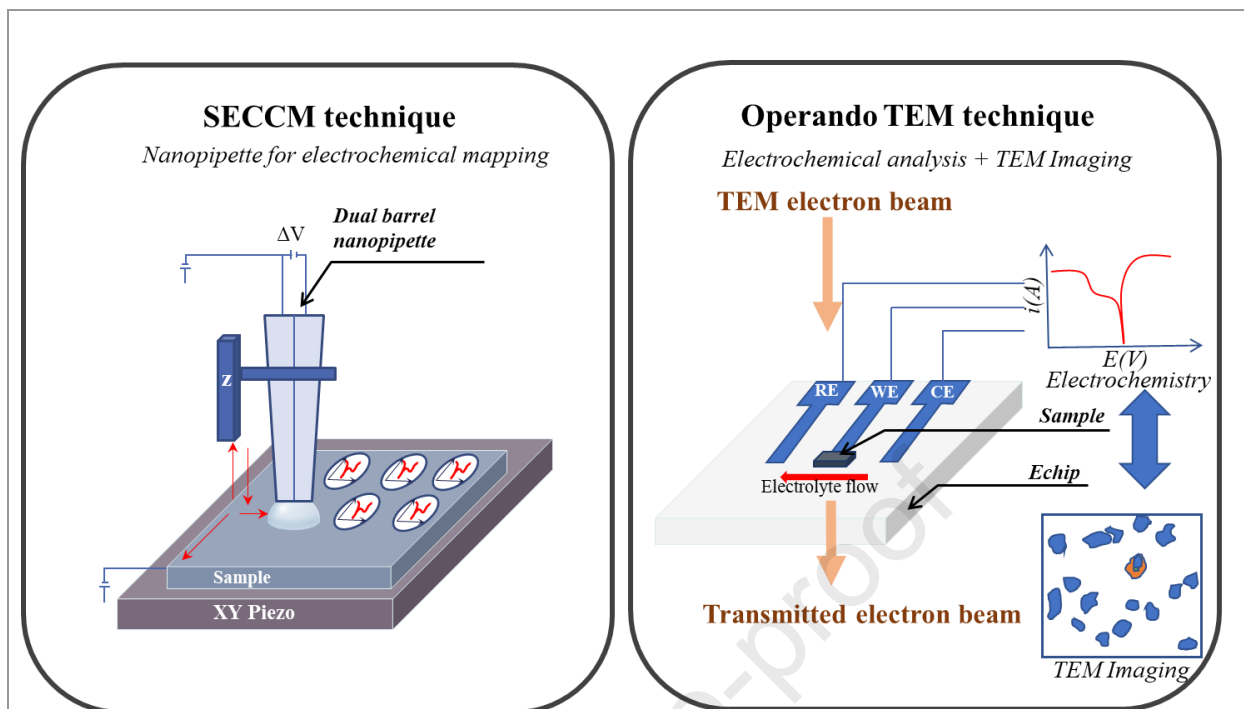
159           Although nanoscale electrochemical measurement can be performed today using scanning  
160 electrochemical microscopy (SECM), SECM measurement usually requires the use of a redox mediator  
161 that could alter the overall corrosion mechanism. Recently, a nanoscale electrochemical setup 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 O<sub>2</sub> ingress into  
171 the droplet if the O<sub>2</sub> 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.*, H<sub>2</sub> 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  $\mu\text{m}$  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  $\mu\text{m}$ -thick E-  
190 chip containing a 5  $\mu\text{m}$  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.



**Fig. 3.** Schematic description of the principle of (a) SECCM technique, consisting of a dual (or single) barrel probe, filled with an electrolyte and quasi-reference counter electrodes. Probe positioning is performed by monitoring the ion current across the meniscus between the two barrels. The nanometer sized probes would allow **direct mapping and establish a** correlation between **nanostructure** characteristics and local reactivity to help identify potential corrosion initiation sites. (b) For *operando* TEM techniques (LP-TEM), the TEM lamellae prepared by focused ion beam technique is placed in the E-chip and welded to the Pt working electrode. The E-chip is then integrated into a TEM sample holder consisting of two electrolyte inlets and one outlet. **Such coupling allows a direct visualization of corrosion initiation mechanisms at the nanometer level.**

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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

224 **Acknowledgement**

225 The authors acknowledge financial support from Sorbonne Université and the Centre National de la  
226 Recherche Scientifique (CNRS), France.

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Journal Pre-proof

229 **References**

230 \* of special interest

231 \*\* of outstanding 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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