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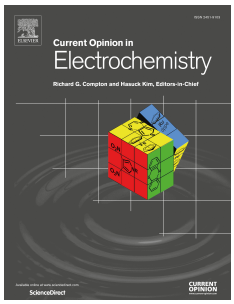
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Current state of electrochemical techniques and corrosion rate analysis for next-generation materials

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Keywords: Corrosion rate; electrochemical techniques; new generation alloys

Abstract

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

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Introduction

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

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

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

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

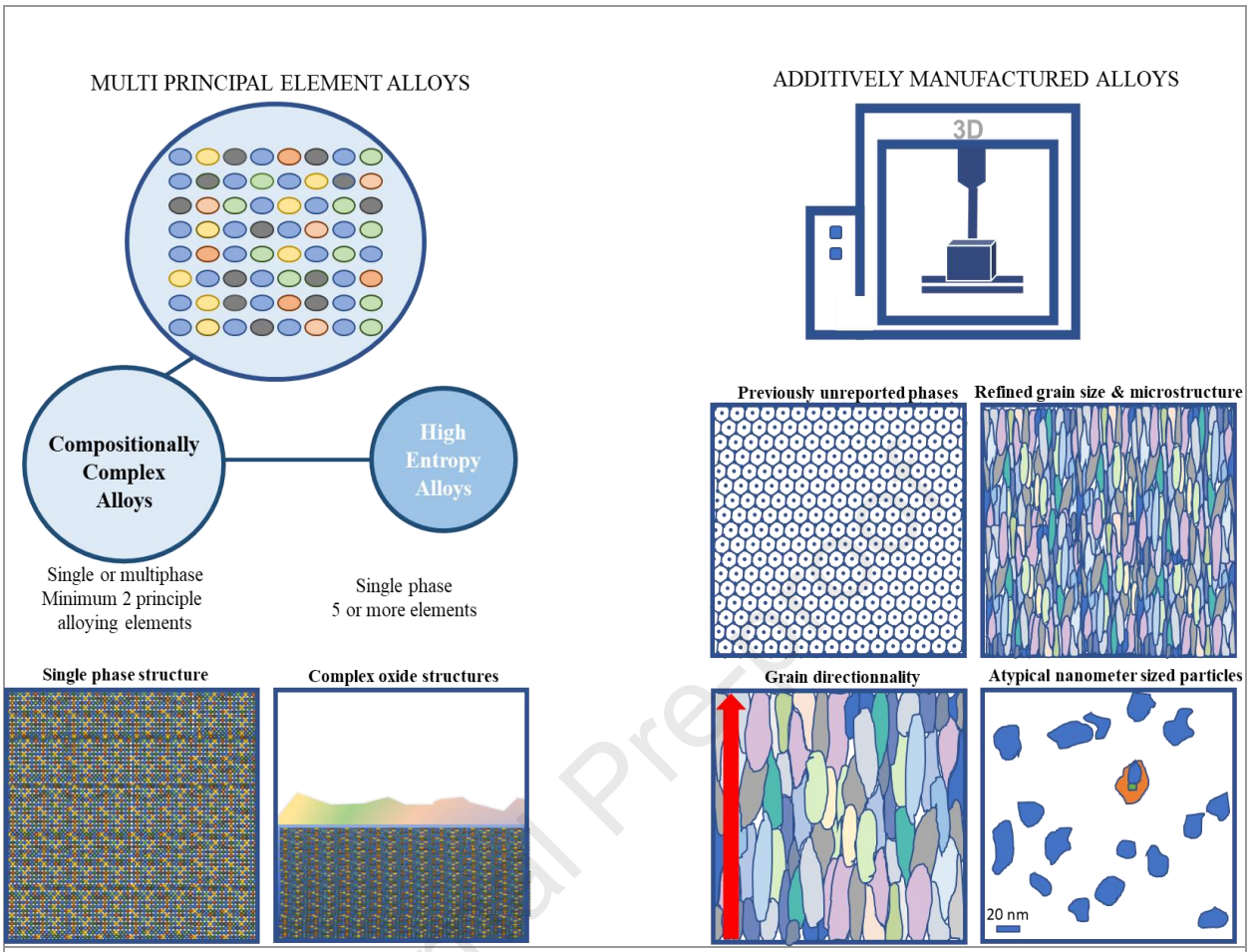


Fig. 1. Schematic illustration of the microstructural characteristics of MPEAs and AM alloys. MPEAs, including high entropy alloys (HEAs), can be single phase multi-element solid solutions and are known to have complex oxide structures. AM alloys have been characterized to exhibit a refined grain size and microstructure with previously unreported phases such as quasicrystals, and grain directionality due to the high solidification rate of the manufacturing process and atypical nanometer sized particles.

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

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

Conventional metal oxidation and passivity models

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

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

Validity of corrosion rate determination: currently used techniques

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

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

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

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

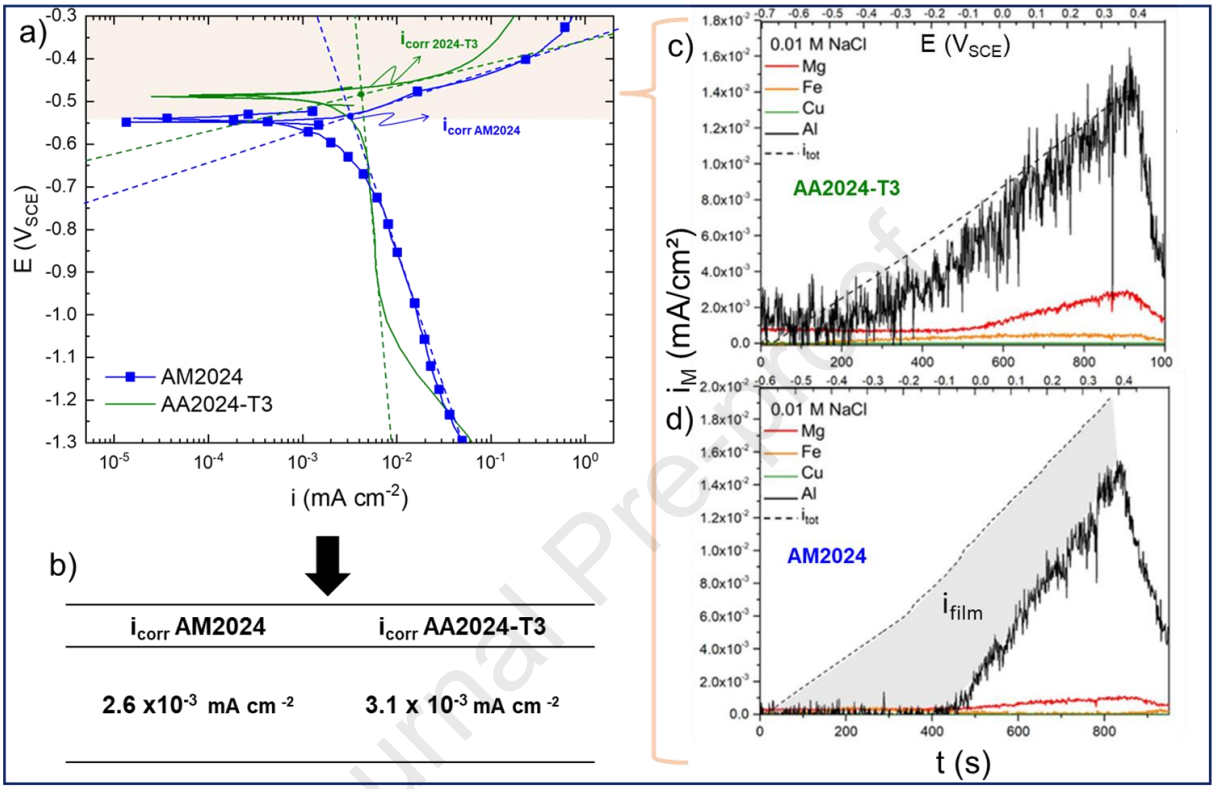


Fig. 2. (a) Potentiodynamic polarization curves of the conventional AA2024-T3 alloy and AM2024 alloy in 0.01 M NaCl with 1 mV/s scan rate. Tafel extrapolation indicates very similar corrosion rates for the two alloys. However, the AESEC anodic polarization curve (indicated by the pink rectangle) for 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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Table 1. Summary of the microstructural specificities of each alloy system and their potential impact on mechanisms interpretation.

Conventional alloys	MPEAs	AM alloys
• 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).	• 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.	• 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].

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

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

Local electrochemistry for MPEA and AM alloys: current limitations

Despite the technical advances, only limited studies on the MPEAs or AM alloys using local electrochemical techniques have been reported to date. Recently, the scanning vibrating electrochemical technique (SVET) technique has been used to investigate a micro-galvanic corrosion between the two eutectic phases of an AlCoCrFeNi MPEA with a 500 nm level step size scans [33]. The SVET technique generally visualizes a real-time the local cathodic and anodic reactions by the potential difference in a solution between a vibrating conductive probe and the sample of interest [34, 35, 36]. Theoretically, it can identify the location of half-reactions and quantify their associated corrosion rates. However, a few technical limitations, such as trade-off sample size [37] and surface topography, could affect the potential measurement leading to an error in quantitative analysis. In addition, real-time corrosion rate determination using this technique for the MPEAs and AM alloys will be significantly influenced by the experimental protocol. For example, high vibrational amplitude may provide an artifact signal due to the accelerated O_2 reduction reaction which is often the rate-determining diffusion-controlled step, giving an incorrect overall corrosion rate [38, 39]. The SVET should be carried out more systematically to the MPEAs and AM alloys considering these limitations to investigate the local corrosion processes.

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

Although nanoscale electrochemical measurement can be performed today using scanning electrochemical microscopy (SECM), SECM measurement usually requires the use of a redox mediator that could alter the overall corrosion mechanism. Recently, a nanoscale electrochemical setup equipped with nano-pipette imaging probe known as scanning electrochemical cell microscopy (SECCM) has been used to monitor local electrochemical events [40, 41]. This concept resembles the electrochemical droplet cell used to visualize anodic and cathodic reactions, in which a nanometer sized mobile meniscus (down to ~ 30 nm [42, 43]) is positioned on the alloy surface (**Fig. 3**.). The SECCM technique was applied to investigate the reactivity of each crystallographic orientation on a polycrystalline alloy defining a structural factor that governs the corrosion mechanism [44]. However, the SECCM technique applied to corrosion studies is still limited to low carbon steel (using a 2 µm probe) and simple systems such as polycrystalline Zn to date [40, 41, 45, 46, 47]. In addition, several technical challenges remain. For example, it has been shown that the exposed surface is often non-reproducible and evolves with reaction time, *e.g.*, by O_2 ingress into the droplet if the O_2 reduction reaction is the dominant cathodic reaction, leading to a significant surface alteration during measurement [48]. The stability of the probe can be affected by the formation of corrosion products or the formation of gas bubbles (*e.g.*, H_2 reduction reaction) during the measurement. Moreover,

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

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

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

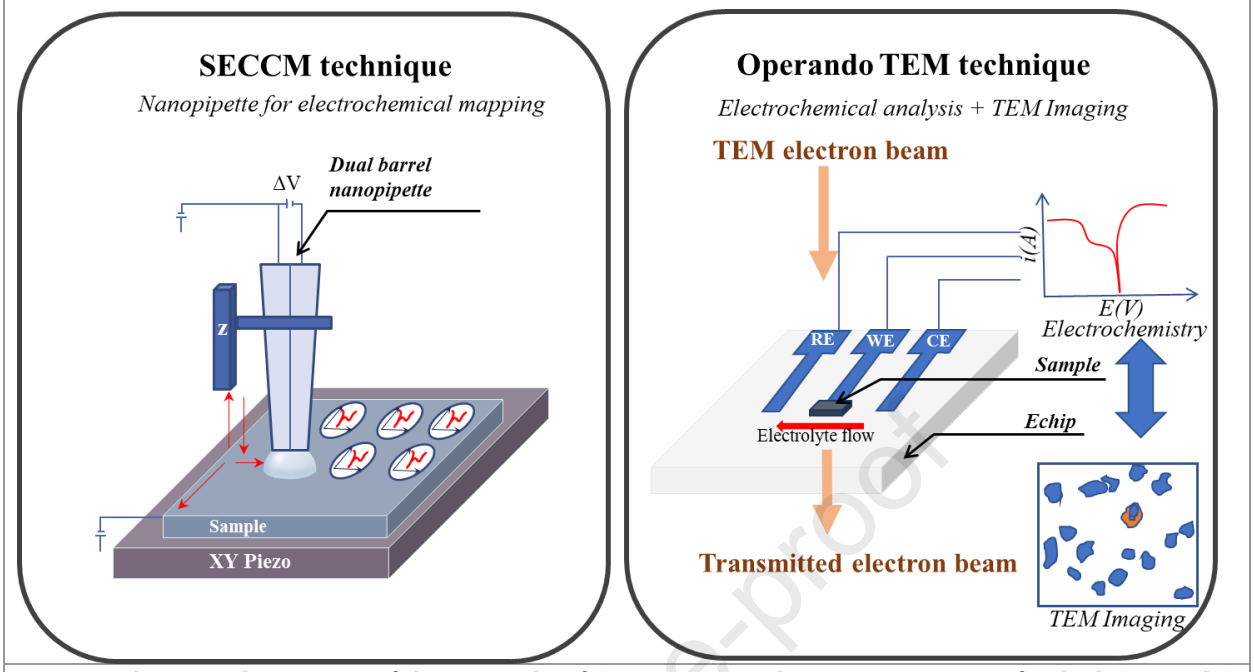


Fig. 3. Schematic description of the principle of (a) SECCM technique, consisting of a dual (or single) barrel probe, filled with an electrolyte and quasi-reference counter electrodes. Probe positioning is performed by monitoring the ion current across the meniscus between the two barrels. The nanometer 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 o*perando* 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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Perspectives and closing remarks

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

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

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

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Conflict of interest statement

Nothing declared.

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229 **References**

230 * of special interest

231 ** of outstanding interest

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Declaration of interest statement

Nothing declared.

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