On-line inductively coupled plasma-atomic emission spectroelectrochemistry: Real-time element-resolved electrochemistry

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Abstract

Electrochemical techniques are coupled with inductively coupled plasma atomic emission spectrometry (ICP-AES) for in-line electrolyte analyses. In this way, a direct measurement of the elemental dissolution rates in real-time or element-resolved electrochemistry can be carried out, complementary to conventional electrochemical measurements of current and potential. This methodology can be used to obtain the element-specific reaction mechanisms under either spontaneous or polarized conditions up to part-per-billion level resolution with applications in diverse domains of corrosion science and interfacial reactivity. This review aims to summarize recent research activities using ICP coupled with other analytical techniques to answer specific questions on the mechanism of degradation of materials in aqueous or organic environments including the dissolution of metal oxides, catalysis, reaction stoichiometry, electrochemical kinetics, and photoelectrochemical reactivity.

Keywords: AESEC; ICP-AES; kinetics; catalysis,

Introduction

Electrochemical methods and concepts are commonly used to measure and interpret interfacial electron exchange processes. The total current (i_e) is a remarkable measurement of the rate of electron exchange and can be obtained with an exceptional degree of accuracy and time resolution. However, in addition to the rate of electron exchange, often we would like to know how the current is distributed among the various elements of a material, distinguish oxide formation from dissolution, separate the anodic and cathodic partial process, observe non-faradaic reactions such as oxide dissolution, particle detachment, or measure dissolution rates at open circuit when the faradaic current is by definition equal to zero.

To obtain element-resolved electrochemical responses (*i.e.*, decoupling elemental anodic dissolution from the total electrochemical current, i_e), spectroelectrochemical methods have been developed coupling an electrochemical flow cell with ICP-AES (AESEC, atomic emission spectroelectrochemistry) or mass spectrometer, ICP-MS, (ASEC, atomic spectroelectrochemistry)[1,2] and have been extensively reviewed.[3,4] In this review, recent advancements in coupling the basic spectroelectrochemical techniques with other analytical techniques are highlighted, while also discussing some of the novel applications of ICP-MS for electrocatalysis. A schematic image illustrating the principle of on-line ICP-AES measurement (*i.e.*, AESEC) coupled with other analytical techniques is presented in **Fig. 1**.[1,3,5]

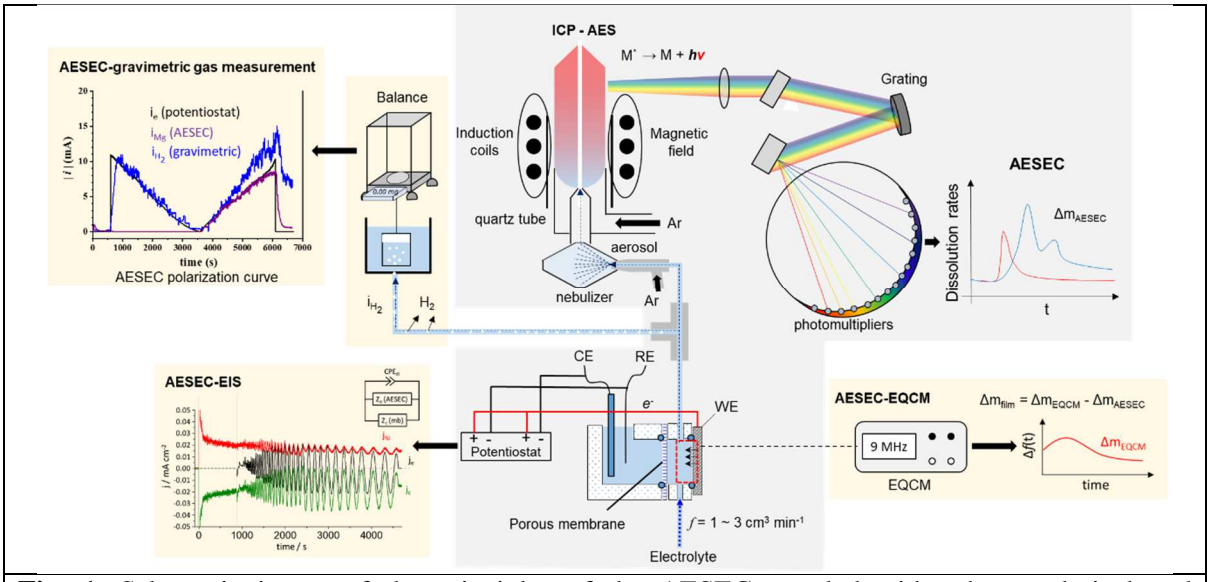

Fig. 1. Schematic image of the principles of the AESEC coupled with other analytical and electrochemical techniques. The electrolyte containing dissolved species from the (electro)chemical reaction is transported to an Ar source plasma, then the dissolved species M is atomized and exited to an energy state of M*. The excited atom M* emits electromagnetic radiation with an element-specific wavelength when it decays to the ground energy state. In the case of the ASEC (ICP-MS),[2] the free ions produced in the plasma are separated by the mass-to-charge ratio with a quadrupole mass spectrometer (not shown here). The intensity of the emitted radiation or ions may be calibrated to determine the concentration of the original solution.

AESEC coupled with other analytic techniques for aqueous corrosion

The AESEC technique provides real-time elemental dissolution rate profiles for multiple elements simultaneously with corresponding electrochemical measurement and/or control of potential and current.[1,3,4,6] For example, an open circuit AESEC dissolution profile gives the contribution of each element to the overall spontaneous corrosion rate simultaneously with the open circuit potential trend, frequently allowing a more precise interpretation of the latter. This *operando* technique has been used in the field of aqueous corrosion of different alloys such as stainless steels,[1,7] bipolar plates,[8] Ni-,[9,10] Al-,[11,12] Mg-,[13,14] Zn-,[15,16] Cu-based alloys,[17,18] multi-principal element alloys, [19,20,21,22,23,24] additively manufactured alloys,[25] noble metals,[26,27,28] surface pretreatment,[29,30,31,32] and electrochemical texturing of thin films for photovoltaic applications (ASEC)[33] which have been reviewed elsewhere.[2,3,4]

Limitations persist such as a lack of direct information[a1] on the deposition kinetics of surface films (*e.g.*, oxides, coatings), quantification of gas formation, difficulty in determining oxidation states, etc. Recent developments have adopted the coupling of AESEC to a few other analytical techniques to overcome these challenges. This section introduces the readers to such advances involving the coupling of the AESEC technique for different applications beyond aqueous corrosion research.

AESEC-gravimetric H_2 measurement

The hydrogen evolution reaction (HER) can occur when a metallic material is exposed to atmospheric or aqueous environments leading to surface defects. This is critical in the case of alloy coatings because local damage to the coating causes a galvanic coupling between the alloy coating and the metal substrate, resulting in an enhanced HER over a large applied cathodic potential. In the case of Mg-based alloys, the evolution of hydrogen during the dissolution limits the use of Mg-based alloys as anodic material in batteries or sacrificial anodes, as well as the application of biocompatible alloys. The HER acts as a parasitic reaction in these applications, reducing battery efficiency and causing defects when used as bio-implants.

Novel experimental protocols for the real-time quantification of the HER have been developed with AESEC coupled with time-resolved volumetry[34] and more recently, with gravimetric H_2 measurement using analytical grade balance.[35] The gravimetric H_2 measurement coupled with the AESEC technique (**Fig. 1**) can give complete stoichiometric information during the reaction by providing the anodic component (i_a, AESEC), the cathodic component (i_c, gravimetric H_2 measurement), and the total charge (i_e, potentiostat). This coupling was applied to a galvanized steel in HCl where the elemental dissolution and HER rate profile were obtained with several kinetic regimes including the dissolution of the alloy coating, the dissolution of the nanometric Fe_2Al_5 intermetallic layer, and the dissolution of the steel substrate.[36] This methodology was also used to

[a] It could be obtained indirectly by mass-charge balance in some cases.

understand the stoichiometry of anodic hydrogen evolution of Mg alloys (*i.e.*, negative difference effect, NDE) as described in **Fig. 2**.[37] Using this novel coupling, it was demonstrated that electrochemical dissolution occurs through an intact Mg-based corrosion product film while HER occurs independently in regions where the film breaks down induced by anodic polarization.

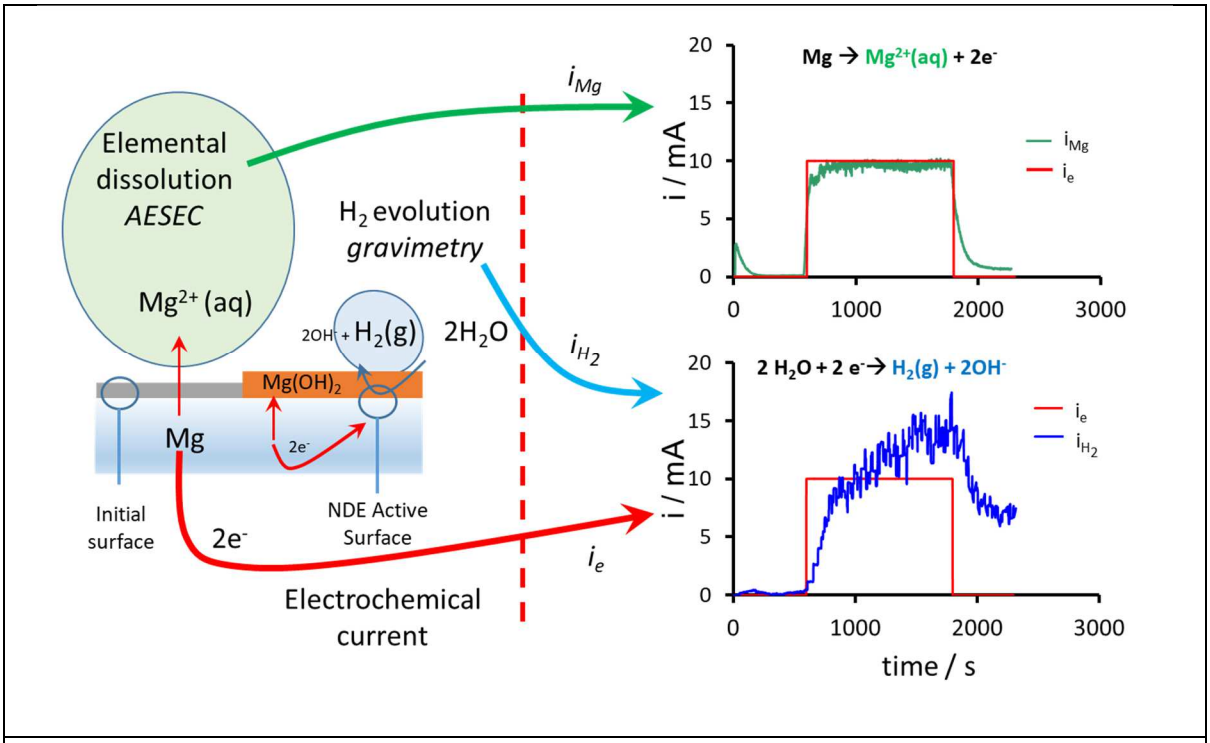

Fig. 2. AESEC-gravimetric H_2 measurement for nominally pure Mg in a 0.1 M NaCl environment, demonstrating the quantification of the negative difference effect (NDE). Adapted from.[37]

AESEC-electrochemical quartz microbalance

The electrochemical quartz microbalance (EQCM) monitors mass changes at the reaction interface with less than one monolayer level (ng cm^{-2}), making it useful for the quantification of (electro)deposition processes.[38] Coupling AESEC with EQCM measures simultaneously the real-time mass changes caused by insoluble film formation (deposition) and the element-resolved dissolution.[39,40] In this way, the total mass change (mass gain + mass loss) can be monitored by EQCM (Δm_{EQCM}), and mass change caused by dissolution (mass loss) can be directly measured by AESEC (Δm_{AESEC}), yielding the film formation rate as $\Delta m_{film} = \Delta m_{EQCM} - \Delta m_{AESEC}$ (**Fig. 1**). This coupling can be used to investigate the elemental contribution of the conversion coating formation

process[41,42] which involves simultaneously the substrate (and/or the film) dissolution and the film formation reactions.

An example of the use of combined AESEC-EQCM is given in **Fig. 3** to determine the stoichiometry and dissolution rate of Zn-phosphate conversion coatings in an alkaline solution.[39,43] Alkaline resistance is an important property of the conversion coating which may encounter an alkaline environment either during the cathodic deposition of a primer layer or during underpaint corrosion by a mechanism of cathodic delamination. For the mono-cation case (**Fig. 3(a)**), AESEC technique permits a clear characterization of the stoichiometry: first there is an equimolar dissolution rates of the Zn^{2+} and PO_4^{-} observed for t < 180 s confirming the stoichiometry of the reaction as follows:

$$Zn_3(PO_4)_2{\cdot}4H_2O + 2OH^- \rightarrow 2Zn^{2+} + 2PO_4^{3-} + 4H_2O + Zn(OH)_2 \quad [1]$$

For t > 180 s, the Zn dissolution rate exceeds that of P due to the dissolution of $Zn(OH)_2$ forming $Zn(OH)_4^{2-}$ by $Zn(OH)_2 + 2\ OH^- \rightarrow Zn(OH)_4^{2-}$. The mass change caused by the $Zn(OH)_2$ formation, $\Delta m_{Zn(OH)_2}$, is calculated by the difference between Δm_{EQCM} and Δm_{AESEC}, given in the right part of **Fig. 3**. The $\Delta m_{Zn(OH)_2}$ transient in **Fig. 3(a)** indicates the $Zn(OH)_2$ formation coupled with its dissolution; thus the mass of the $Zn(OH)_2$ passes through a maximum around t = 180 s.

Figs. 3(b) and **3(c)** are the bi-cations cases showing the effect of Ni^{2+} and Mn^{2+}, respectively, often added to the conversion coating bath to improve the physical and chemical properties of the coating.[42] In both cases, the dissolution rate of the phosphate conversion coating is markedly reduced due to the formation of more stable $Mn(OH)_2$ that was also detected by *in situ* Raman spectroscopy.[44]

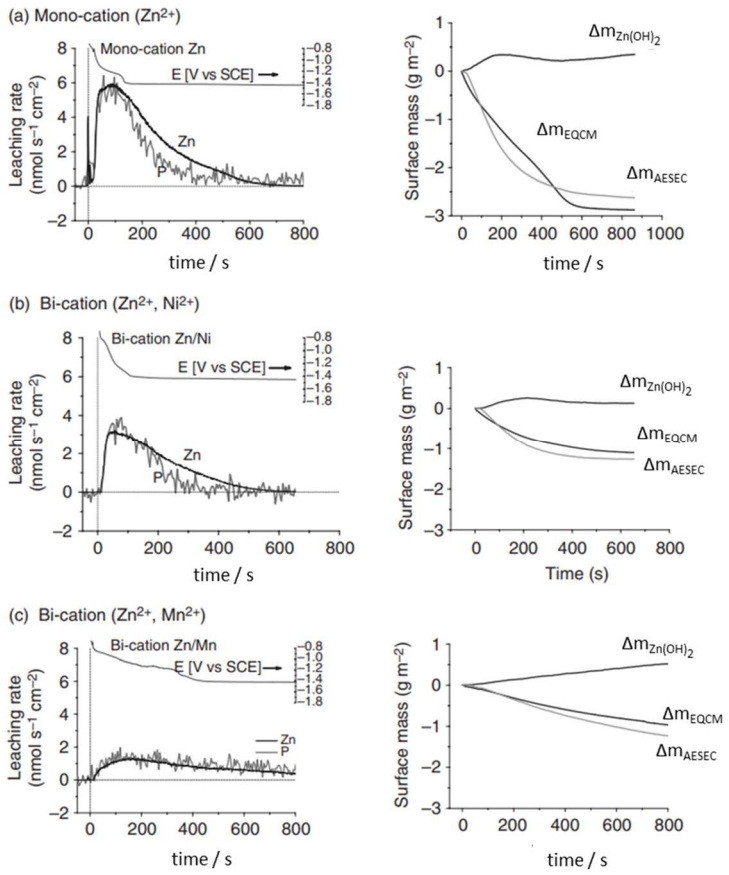

Fig. 3. Left column: elemental dissolution (leaching) rates profiles, right column: mass changes monitored by EQCM (Δm_{EQCM}) and AESEC (Δm_{AESEC}) for various phosphate layer compositions for the Zn-phosphate conversion coating formation reaction in deaerated 0.1 M NaOH solution. (a): Mono-cation (Zn^{2+}); (b) bi-cations (Zn^{2+}, Ni^{2+}); and (c) bi-cations (Zn^{2+}, Mn^{2+}). The $\Delta m_{Zn(OH)_2}$ curves represent the mass of the hydroxide intermediate ($\Delta m_{EQCM} - \Delta m_{AESEC}$). Adapted from.[39]

AESEC-electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) can give kinetic information about a steady-state reaction system. Interfacial properties obtained from the EIS spectra are often used to quantify the kinetic processes including corrosion rates, resistance, and thickness of the surface film.[45] Coupling EIS with AESEC provides element-resolved kinetic information.[46,47] It also allows to distinguish the anodic and cathodic dissolution mechanisms on the one hand, and between dissolution and film formation on the other.[48,49] Recently, element-resolved EIS plots of pure Ni and Fe have been investigated using the AESEC-EIS methodology to quantitatively distinguish anodic (metal

dissolution) and cathodic (HER) reactions in sulfuric acid media.[50] In this case, the intermediate short-lived adsorbed species (*e.g.*, FeH_{ads}, NiH_{ads})[51] could be ascertained by calculating the impedance of each reaction as:

$$Z_{j_M} = \left| \Delta E/\Delta j_M \right| (\cos \varphi + j \sin \varphi) \quad [2]$$

where Z_{j_M} is the impedance of equivalent elemental current density j_M (M can be an element or H_2) and φ is the phase angle of the EIS measurement. In **Eq. 2**, Δj_M was determined from the analog sinusoidal signal of j_M obtained by the AESEC data acquisition system, and used as a transfer function between the electrochemical and spectroscopic measurements.[52] In the absence of insoluble species formation, this permits the calculation of the anodic component of impedance (Z_a) from the electrochemical dissolution, and the cathodic component of impedance (Z_c) from the reduction of the electrolyte, as described in **Fig. 1**. In this case, element-resolved EIS plots (*e.g.*, Nyquist or Bode) may be obtained to shed light on elemental dissolution kinetics. A low-frequency loop in the Nyquist diagram is often attributed to the oxidation of this intermediate species or hydrogen evolution.[50] The element-resolved Bode plot for pure Ni and pure Fe in sulfuric acid showed that the low-frequency impedance is dominated by the cathodic impedance Z_c.[50]

A(E)SEC for other fields of electrochemistry

Photoelectrochemistry and catalysts

Photocorrosion of metal oxides is a non-negligible process for photoelectrochemical water splitting for energy applications, influencing the durability and overall efficiency of devices. Conventional electrochemical measurements to investigate the degradation mechanism of the photoelectrochemical water splitting are limited because of either insufficient resolution due to stable metal oxide materials yielding non-significant changes in electrochemical response or lack of elemental-specific contribution to photocorrosion.[53] To this end, electrochemical measurements coupled with on-line ICP-MS (ASEC) using an electrochemical scanning flow cell have been used to

monitor the photoelectrochemical responses of semiconducting oxides.[54,55,56] For example, it was reported that Zn dissolution from polar ZnO was accelerated by the UV irradiation at pH = 8 whereas nonpolar ZnO showed significantly less photocorrosion, thus demonstrating the possibility of direct quantitative monitoring of the photon-induced dissolution of the facet-tuned surface film.[53] Another example involves significant dissolution of WO_3 which was monitored during photoelectrochemical water splitting where the dissolved W was found to be proportional to the applied charge.[52]

Elemental dissolution profiles of metal oxide catalysts were also investigated by ICP-AES coupled with an oxygen sensor to measure the catalytic activity of the oxygen evolution reaction (OER).[57] In this way, elemental dissolution rates of Ni and Co from $NiCoO_2$ in 1 M KOH; Co from Co_3O_4 in 1 M KOH; and Ir from IrO_2 OER catalyst in 0.1 M $HClO_4$ could be simultaneously monitored with potential vs. time during galvanostatic hold at 10 mA cm^{-2} for ~8000 s.

The anodically formed (at different time durations) topmost atomic layers of IrO_3 for the OER were characterized simultaneously by ICP-MS to investigate the stability and activity of the material during and toward the reaction.[58] The result was then further complemented by combined *ex situ* characterizations, demonstrating that longer anodic polarization increases the stability at the detriment of decreased catalytic activity.[59] All this demonstrates the capability of *in situ* ICP-photoelectrochemistry to investigate the stability of the catalyst and co-catalyst materials in various environments.

Battery materials

The analysis of the activity and stability of the transition metal-based oxide materials for energy application relies heavily on the conventional electrochemical test and *ex situ* electrolyte analysis for the quantification of the dissolved species. In this case, dynamic elemental reactivity during charge-discharge cycles cannot be directly monitored. The stationary probe rotating disk electrode (RDE) coupled to ICP-MS (SPRDE-ICP-MS) was introduced to simultaneously monitor the metal oxide dissolution and deintercalation kinetics of the working cations.[60] This technique also makes it possible to monitor the degradation of the organic solvent, usually not possible *via* conventional electrochemical measurements. Co dissolution from $LiCoO_2$ cathode material in 1.2 M

177 $LiPF_6$ in 3:7 ethylene carbonate/ethyl methyl carbonate organic solvent was quantitatively evaluated
178 by SPRDE-ICP-MS using an RDE-specific stationary probe, organic environment-appropriate tubing
179 and nebulization equipment. This method was also used to monitor the kinetics of dissolved Mg^{2+}
180 cations throughout the $MgCr_2O_4$ deintercalation process for Mg-ion batteries in 0.2 M LiTFSI.[60]

181

182 *Surface pretreatment*

183 Non-faradaic particle release during corrosion or surface treatment processes cannot be
184 generally detected by conventional electrochemical measurement and has been often overlooked.
185 Over the years, non-faradaic particle release has gained considerable interest, particularly in the
186 context of dealloying and surface treatment of Al alloys.[61] AESEC has demonstrated the ability to
187 provide quantitative analysis on non-faradaic processes. Element- and time-resolved particle analysis
188 by the AESEC technique is possible with fast data acquisition (1000 Hz level) detecting the element-
189 specific transient events within this time frame.

190 Mokaddem *et al.* observed the surface detachment of Cu-rich particles while monitoring the
191 potential-controlled local dissolution of an Al-Cu-Mg alloy in NaCl.[62] Serdechnova *et al.* qualitatively
192 measured Al particles of various nominal sizes released from Al particle-enriched patinas.[63] Gharbi *et*
193 *al.* also qualitatively measured the release of different types of intermetallic particles during alkaline
194 etching of an AA2024.[29,64] Statistical analysis revealed a strong correlation between different
195 elemental signals and intensities that were found to be consistent with expected intermetallic particles
196 such as Al_2CuMg and Al_7Cu_2Fe (**Fig. 4**). These findings are promising in the context of materials
197 design because they demonstrate the possibility to analyze a large population of particle composition
198 and get access to alloy composition (intermetallic size, composition, and proportions).

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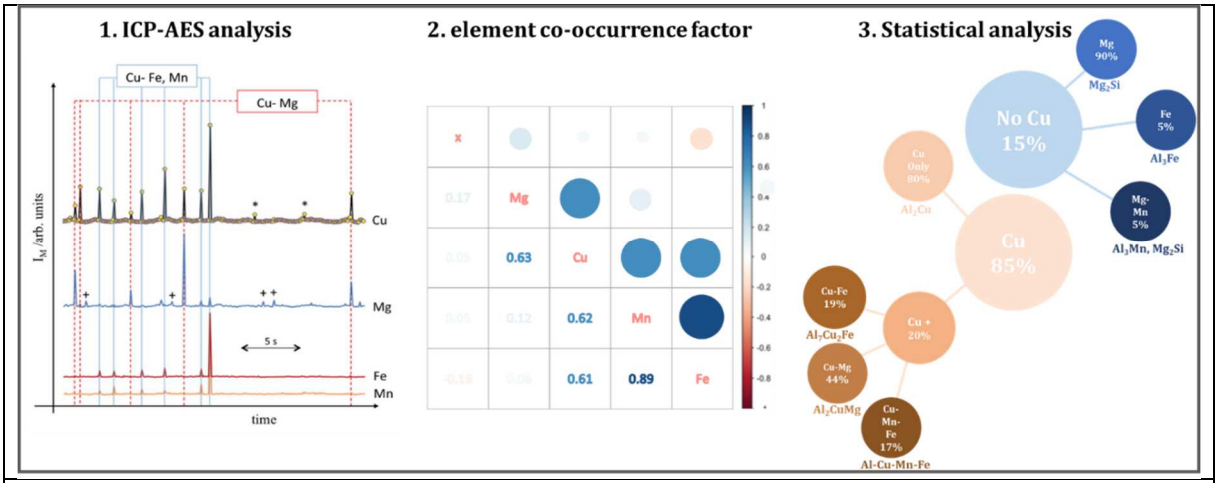

Fig. 4. Schematic illustration of the AESEC elemental dissolution rate transients for Cu, Mg, Fe, and Mn of an AA2024 alloy exposed to 1.2 M NaOH at T = 60°C. The data was acquired at 10 Hz to provide greater temporal resolution on transient events and each peak corresponds to a transient particle release event. The statistical analysis of such peaks revealed a strong co-occurrence between certain elements and their intensities. For example, there were frequent appearance of simultaneous Mg and Cu peaks, probably due to Al_2CuMg particle release. The high-intensity peaks were linked to large intermetallic particles with stoichiometry correlated to what is reported in the literature. The figure is taken from.[63]

Perspectives and closing remarks

AESEC and electrochemical methods can be adapted with a few other complementary on-line techniques to answer contemporary scientific questions, such as the degradation mechanism of materials used in energy applications. Although the current experimental setup of AESEC is somewhat limited to macroscopic scale electrochemical analysis[65], this technique could however be extended to the monitoring of localized reactions, for example by coupling it with atomic force microscopy.[66] The determination of the oxidation states could also be carried out by coupling with ion exchange chromatography[67] although these couplings remain *ex situ* to date. For single particle analysis, several technical aspects must be optimized, such as the injection system (nebulizer and spray chamber types). In addition, the atomization process of single particles and the effect of particle composition on signal intensity are still not well understood and thus require further research. Finally, a better understanding of the hydrodynamics of the electrochemical flow cell used in the AESEC technique can be obtained by numerical modeling.[68]

Conflict of interest statement

Nothing declared.

Acknowledgment

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