HAL
open science

Unprecedented reactive electro-mixing reactor: Towards synergy between micro- and macro-reactors?

Emmanuel Mousset

To cite this version:

Emmanuel Mousset. Unprecedented reactive electro-mixing reactor: Towards synergy between micro- and macro-reactors?. Electrochemistry Communications, 2020, 118, 10.1016/j.elecom.2020.106787 . hal-02993202

HAL Id: hal-02993202

https://hal.science/hal-02993202v1

Submitted on 6 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Electrochemistry Communications 118 (2020) 106787

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Unprecedented reactive electro-mixing reactor: Towards synergy between micro- and macro-reactors?

Emmanuel Mousset*

Laboratoire Réactions et Génie des Procédés, Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

ARTICLE INFO

Keywords:
Electro-rotation
Microfluidic
Macro-reactor
Reactive electro-mixing
Thin film
Water treatment

ABSTRACT

Over the last century, electrochemistry has contributed to societal progress through the development of electrochemical industrial processes. Since the first battery was proposed by Alessandro Volta in 1799, the vision of the electrochemical cell has not changed significantly: static electrodes (or semi-static in rotating disk and cylinder systems) are immersed in an electrolyte while the solution is either stirred for better homogenization or pumped between or through the electrodes. This work intends to induce a paradigm shift in the design of electrochemical cells that could have tremendous positive impacts on the mechanisms (e.g. transfers), the process efficiency and the scalability of electrochemical processes. It is proposed to set whole thin film electrochemical cells in motion within a stirred tank macro-reactor, with the aim of synergistically combining the properties characteristic of the micro-scale in thin film reactors with those of the macro-reactor.

This paper highlights the superiority of the unprecedented "reactive electro-mixing" reactor in water treatment, i.e. 1.32 times higher degradation efficiency and 20 times lower energy requirement than a conventional filter-press cell. It further announces the birth of a new "reactive electro-mixing" sub-discipline that should lead to many other scientific studies and industrial applications.

1. Introduction

Over the last century, electrochemistry has contributed to societal progress through the development of industrial processes for electrosynthesis [1], electroanalysis [2,3] and the implementation of renewable systems for energy storage, i.e. redox flow battery and fuel cell [4,5]. More recently, electrochemical technologies have emerged in the area of environmental protection by using the electrolytic mode to generate very strong oxidizing agents capable of degrading and mineralizing biorecalcitrant organic pollutants, e.g. emerging contaminants, from industrial and urban wastewater treatment plants (WWTPs) [6–9], with the aim of reusing the treated water.

Alessandro Volta contributed greatly to the early development of electrochemistry by proposing the first battery in 1799. Since then, much effort has been devoted to identifying the main parameters that control and increase the charge and mass transfers (the factors involved in the efficiency of heterogeneous reactions at electrode surfaces), in order to improve the efficiency of electrochemical processes.

It has been shown that in many electrochemistry applications, mass transport is the rate-limiting step, especially in dilute media. Therefore, a quest for mass transfer intensification was launched, by playing particularly with the electrochemical cell design and the physical properties of the electrode material. Paul Léon Hulin patented the "electrolyfiltration" technology in 1893, involving a porous electrode that enabled the chlor-alkali process by electrosynthesis from an aqueous solution of sodium chloride [10]. Instead of using parallel plate electrodes, this "flow-through" process permitted the electrolyte to flow through the electrodes and can be viewed as an important revolution in electrochemical engineering. The great advantage of this system is that it operates with a dilute solution which implies the implementation of a low current density (j), bearing in mind that the limiting current density (j_{lim}) is proportional to the concentration in bulk solution (C_{sol}) (Eq. (1)) [11]. This equation is derived from the Butler-Volmer theory assuming an infinite value of charge transfer rate constant and Faraday's law.

$$j_{lim} = \frac{i_{lim}}{A} = n_e F k_m C_{sol} \tag{1}$$

where A is the electrode surface area, F is the Faraday constant and n_e is the number of electrons exchanged.

Eq. (1) shows that an electrode with a high surface area is required in order to obtain a low current density with a low concentration of the targeted compound in solution (C_{sol}). Applying a higher current density would decrease the faradic yield because not all of the current would be employed in the targeted compound transformation.

* Address: 1, rue Grandville – BP 20451, 54001 Nancy cedex, France.
E-mail address: emmanuel.mousset@univ-lorraine.fr.

https://doi.org/10.1016/j.elecom.2020.106787
Received 25 June 2020; Received in revised form 8 July 2020; Accepted 8 July 2020
Available online 13 July 2020
1388-2481/ © 2020 The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

In the 1960s and 1970s, electrochemical reaction engineering was developed and allowed the derivation of relations based on the main parameters characterizing electrochemical reactors, i.e. the electrode surface area, the conversion yield (X), the mean residence time (τ) ($\tau = V/Q_V$, where Q_V is the volume flow rate and V is the reactor volume) and the rate of reaction (r) [12–14]. Considering a single electrochemical reaction, this latter parameter depends on the current density, the Faraday constant and the number of electrons exchanged (Eq. (2)), as derived from Faraday's law:

$$r = \frac{j}{n_e F} \tag{2}$$

Considering applications in dilute media, mass transport, defined by the mass transport coefficient (k_m), is the rate-limiting step and the expression of j can be simplified by using Eq. (1). The formulae for conversion yield in a batch reactor (where t is the electrolysis time) (Eq. (3)), a continuously stirred tank (Eq.4) and a plug-flow reactor (Eq. (5)) can be obtained under these conditions [13]:

$$X = 1 - exp\left(-k_m \frac{A}{V} t\right) \tag{3}$$

$$X = \frac{k_m \frac{A}{V} \tau}{1 + k_m \frac{A}{V} \tau} \tag{4}$$

$$X = 1 - exp\left(-k_m \frac{A}{V} \tau\right) \tag{5}$$

These expressions clarify the need to increase A, independent of the reactor volume, and k_m, independent of the flow rate, by optimizing the reactor design and the properties of the electrode material. The benefits obtained since the end of the nineteenth century by using 3D porous materials and flow-through cells could therefore be explained, since these approaches greatly increase A and k_m, respectively. In practice, this theory makes it possible to optimize electrochemical reactors and minimize the cost related to the electrode materials, which is important in the global cost of electrochemical processes [15]. Using these primary formalisms, electrochemical engineers have implemented turbulence promoters and proposed different reactor designs [16–19], e.g. fluidized and packed beds, falling-film cells, flow-through electrodes of expanded metal, submerged multijet cells, and spiral cells (such as the Swiss Roll reactor). In parallel, another innovative design was proposed in the 1950s: rotating disk and cylinder electrodes, which make it possible to control the mass transfer rate and diffusion layer thickness at the electrode/electrolyte interface in laminar flow [20] and turbulent flow [21], respectively. These designs also enabled improvements in mass transport and have found applications in electro-analysis [20], corrosion studies [21], and to a lesser extent in self-pumping systems [22].

Still guided by the objective of transfer intensification, microfluidic thin film electrochemical cells were first proposed in the 1960s [23]. The inter-electrode distances ranged from the micrometer scale to several hundred microns [24]. One of the great advantages of thin film cells is the increased kinetics of the redox cycles of dissolved electroactive species and hence the faradic current. Thin film cells have also more recently been developed in microfluidic versions for environmental applications, especially (since 2010) for water treatment [25]. In emerging electrochemical research applications, transfer intensification still remains important since it is concerned with dilute solutions [26]. Micro-reactors make it possible to (i) reduce the electrode surface area required by increasing the mass transport by 10 to 100 times; (ii) avoid the addition of supporting electrolyte that would constitute another source of pollution and (iii) drastically reduce the cell potential and consequently the energy consumption. However, there is a major drawback with these technologies. Micro-fluidic devices cannot meet the treatment capacity requirements for water treatment applications. Moreover, they cannot operate with suspensions and/or viscous media due to major clogging effects.

Currently, electrochemical reactors are composed of static working electrodes or semi-static working electrodes (2D/3D, porous/non-porous) implemented in rotating disk and cylinder systems, either immersed in electrolyte (when the counter-electrode is static and the solution is likely stirred for better homogenization) or with the electrolyte (self)-pumped between or through the electrodes. This work intends to introduce a paradigm shift in the design of electrochemical cells that could have positive impacts on the mechanism (e.g. transfers), the process efficiency and the scalability of electrochemical processes, especially micro-reactors. It is proposed to set whole electrochemical cells into motion within the medium, with the transport phenomena occurring in the electrolyte being induced by the rotation in space of the so-called "reactive electro-blades". This innovative design, named a "reactive electro-mixing reactor", is intended to address transfer limitations in macro-reactors and low treatment capacity in microfluidic thin film cells, while allowing the possibility of performing electrochemistry in liquid and semi-liquid mixtures (e.g. slurry) with rheologically complex properties. A synergy between micro-reactor and macro-reactor is thus obtained in the unprecedented hybrid system introduced in this paper.

2. Materials and methods

2.1. Chemicals

Sodium sulfate (Na_2SO_4) was provided by VWR International (Fontenay-sous-Bois, France). Acetaminophen (i.e. paracetamol) was supplied by Sigma-Aldrich (Saint-Quentin-Fallavier, France). All the chemicals were of analytical grade and were used as is. The solutions were prepared with ultrapure water from a Purelab® water purification system (Veolia Water, Antony, France) (resistivity > 18 MΩ cm at room temperature).

2.2. Reactive electro-mixing treatment

The key feature of the reactive electro-mixing reactor is an impeller with two blades, designated as "reactive electro-blades" (Fig. 1a). Each blade is formed of a thin film electrochemical reactor. Typical counter-vortex systems are placed close to the wall of the macro-reactor to avoid vortex formation and heterogeneous mixing.

It is important to highlight that this novel method is fundamentally different to existing rotating ring, disk or cylinder electrodes that move according to only one fixed axle, while the counter-electrodes remain static. Rotating electrodes favor mainly axial flow [27], which is not enough to ensure the strong turbulent flow that is required for good mixing, especially for a non-Newtonian fluid. Radial and tangential flows are also needed to increase the turbulent flow to ensure better mixing – this could be obtained using a turbine-like Rushton setup with several blades (Fig. 1a).

The sizing constraints of a Rushton-type mixing tank were therefore adopted as a first approach to the design of this novel type of reactor (Fig. 1a) [27]. Each electro-blade was composed of a porous soft carbon felt cathode (14 cm^2) with a thickness of 5 mm (RVG 2000 by Mersen, Gennevilliers, France) and a perforated (5 mm hole diameter, holes spaced 5 mm apart in length and width) Niobium (Nb) anode (14 cm^2) coated with BDD on both sides (12 μm in layer thickness) (DiaCCon, Fürth, Germany), separated by a perforated (1 mm hole diameter, with holes spaced 2 mm apart in length and width) nylon spacer 500 μm thick (Fig. 1b). This inter-electrode distance was found to be optimal in a previous study on degrading paracetamol [28]. The carbon felt materials were pre-conditioned before use according to a previous protocol [28], to ensure that no impurities were present. The volume of treated solution in the cylindrical, poly(methyl methacrylate) (PMMA) reactor was 4 L and the reactor had an internal diameter (D in Fig. 1a) of 19 cm. Each blade was connected in monopolar mode to a power supply

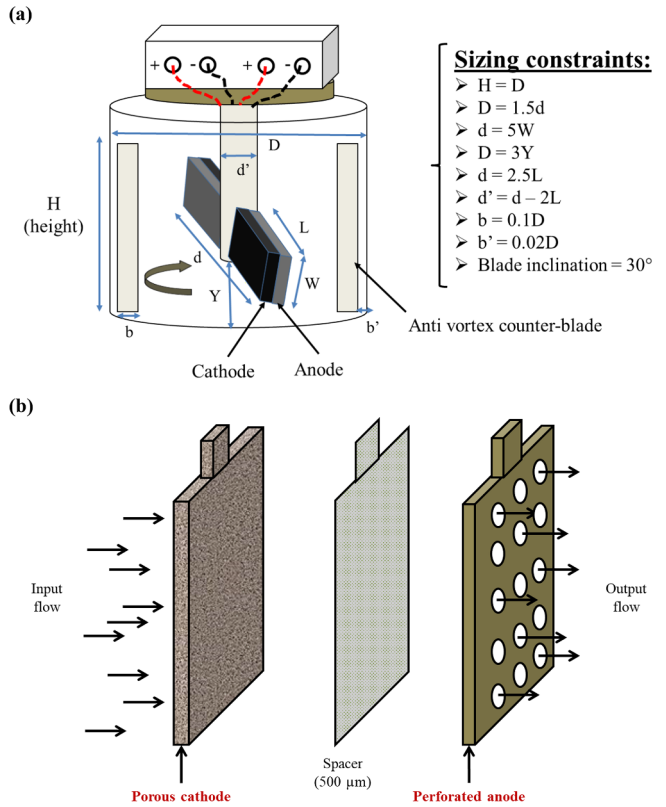

Fig. 1. (a) Schematic diagram of a reactive electro-mixing reactor, including hybrid micro-/macro-reactors as electro-blades; (b) schematic diagram of a flow-through reactive electro-blade.

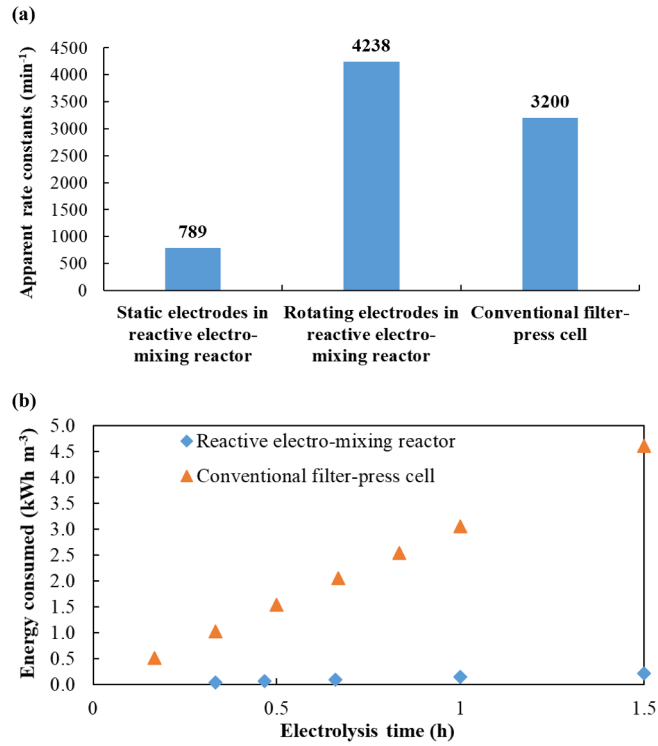

Fig. 2. Comparison of a reactive electro-mixing reactor with a conventional flow-by microfluidic filter-press cell: (a) apparent rate constants for paracetamol degradation after equivalent residence times in three different reactor configurations; (b) energy consumption as a function of electrolysis time. Initial conditions: [Na_2SO_4] = 4 mM; [paracetamol] = 0.1 mM; cathode: carbon felt; anode: boron-doped diamond (BDD), inter-electrode distance = 500 µm; neutral pH, conductivity = 850 µS cm^{-1}.

(HAMEG 7042-5 (Beauvais, France)) with an applied current intensity of 200 mA per electro-blade, as carried out in a previous study [28]. The connection between the static power supply and the rotating electro-blades was achieved using a rotating electrical connector ring (GoTronic, Blagny, France). The connection between the shaft and the electro-blades was established using electrical wires with an insulating sheath made of polytetrafluoroethylene (PTFE) to avoid any reaction of the wires with the media. Contact was made between the wires and the electrode materials via the nylon screw that holds the wires and electrode materials on the shaft. The monopolar mode and the BDD coating on both sides ensured the production of ·OH and therefore the reactions on both the internal side of the thin film cell and the external side of the cell, while keeping the distribution of potential more homogeneous. The rotation speed of the impeller was 35 rpm to ensure good mixing.

This efficiency of this configuration was compared to one without electrode rotation, i.e. with a static electrochemical cell, while the solution was stirred with a magnetic stirrer at 500 rpm (Corning PC-410D) for homogeneous mixing.

In all the systems paracetamol (0.1 mM) was selected as a representative organic biorecalcitrant pollutant in water, and sodium sulfate was added as a supporting electrolyte at a concentration (4 mM) providing a conductivity (850 µS cm^{-1}) representative of that found at the outlet of wastewater treatment plants. The pH of the solution was kept neutral.

The reactive electro-mixing reactor was also compared with a more conventional thin film (500 µm) microfluidic PMMA reactor operated with static electrodes, i.e. carbon felt cathode and BDD anode, whose characteristics have been described in a previous study [28]. The optimal conditions given in the study [28] for paracetamol (0.1 mM) degradation in synthetic wastewater (i.e. an inter-electrode distance of 500 µm and 200 mA (4 mA cm^{-2}) with 4 mM of sodium sulfate supporting electrolyte, neutral pH and a recirculated flow rate of 0.43 L min^{-1} using 200 mL of solution) have been adopted in this article.

2.3. Analytical procedures

A UV–vis spectrophotometer (Anthelie Light, Secomam-Aqualabo, Champigny-sur-Marne, France) was employed to quantify paracetamol, at the maximum absorbance given by wavelength 243 nm [28].

3. Results and discussion

The efficiency of paracetamol degradation in the reactive electro-mixing reactor has been compared in two different configurations: (i) with static electrodes and mixing with a magnetic stirrer, (ii) with rotating electrodes (without a magnetic stirrer). A pseudo first-order model was considered for the degradation of paracetamol and the correlation between the model and the experimental data was in good agreement, with correlation coefficients (R^2) higher than 0.998. This further confirmed that the kinetics is governed by mass transport, which is typically the case in dilute media.

The pseudo first-order rate constants were 789 min^{-1} and 4238 min^{-1} in the first and second configurations, respectively (Fig. 2a). The movement in space of the electrochemical cells led to a greater removal efficiency. This is presumably due to the higher mass transport coefficient in this system.

The results were also compared with those for a conventional flow-by thin film microfluidic electrochemical cell, where the pseudo first-order rate constant was 3200 min^{-1}, which is 25% less efficient than the reactive electro-mixing reactor for an equivalent residence time. In addition, the ratio of electrode surface per volume of treated solution was 7×10^{-3} cm^2 cm^{-3} for the electro-mixing reactor (due to Rushton-type sizing constraints (Fig. 1a)) compared with 0.25 cm^2

cm^{-3} for the static filter-press cell, which is not to the advantage of the new reactor. Therefore, the novel reactor was more efficient, although the surface/volume ratio was much lower. It seems that the electro-mixing device enhances the mass transport, and the movement of the electrodes provides increased contact with the media. This latter feature is particularly important in increasing the removal efficiency when considering heterogeneous mechanisms like advanced electro-oxidation with a BDD anode [26].

An energy consumption comparison was also carried out and is depicted in Fig. 2b. The energy requirements from the power supply were much lower for the electro-mixing reactor than for the filter-press with static electrodes. For example, the electric energy reached 4.6 kWh m^{-3} after 90 min of electrolysis in the conventional cell, while it was only 0.22 kWh m^{-3} for the new reactor. The energy consumption was therefore 20 times higher for the static cell. The electro-mixing reactor with its movement of the electro-blades allowed the cell resistance to be minimized, and the cell potential was also consequently minimized, i.e. 1.5 V per electro-blade against 3 V for the filter-press cell. Moreover, the volume treated per electro-blade (2 L) is much higher than in the filter-press (0.2 L), while the sum of the cell potentials of the electro-blades remains similar to that of the conventional cell. This emphasizes the advantage of inserting micro-reactors – implementing low cell potentials – in a macro-reactor in order to treat much higher volumes without affecting the cell voltage. These results further highlight the possibility of applying this technology in low conductivity media by keeping the energy demand low.

4. Conclusions

The results obtained with a novel reactive electro-mixing reactor were compared with those from a more conventional flow-by micro-fluidic thin film electrochemical cell. The degradation efficiency of paracetamol (selected as representative pharmaceutical pollutant in water) was 1.32 times higher in the electro-mixing reactor. Moreover, the energy requirement was 20 times lower in this novel reactor. It is important to note that even without optimization of the reactive electro-mixing reactor, its efficiency is already better than that of the optimized filter press cell, which suggests interesting perspectives for future research in this area.

Optimization of the proposed design for water treatment purposes could be performed by increasing the surface/volume ratio of the electro-blades, without compromising good mixing. The current density, the number and shapes of the electro-blades could also be optimized and the direction and speed of rotation studied. Research is currently under way on “electro-mixing” theory development and process optimization using (electro)-chemical engineering tools.

This modular reactor should lead to numerous applications dealing with Newtonian and non-Newtonian mixtures, for example in environmental protection (water/wastewater and sludge treatment, soil remediation), electro-analysis, electro-synthesis, electro-mining and corrosion studies. Furthermore, it allows different electrochemical cells featuring electrode materials with different properties in the same reactor, which would make it possible to operate several mechanisms (electro-coagulation/flotation, electro-oxidation/reduction, electro-sorption, electro-deposition, etc) at the same time. This could lead to synergies compared to existing industrial reactor design, especially those involving stacks of cells, which do not permit such simultaneous reactions and operations.

CRediT authorship contribution statement

Emmanuel Mousset: Conceptualization, Methodology, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by “Lorraine University Excellence for Future Leader” (ElRot) fund.

References

[1] S. Bebelis, K. Bouzek, A. Cornell, M.G.S. Ferreira, G.H. Kelsall, F. Lapicque, C. Ponce de León, M.A. Rodrigo, F.C. Walsh, Chem. Eng. Res. Des. 91 (2013) 1998–2020.
[2] M. Mierzwa, E. Lamouroux, A. Walcarius, M. Etienne, Electroanalysis 30 (2018) 1241–1258.
[3] C. Chatard, A. Meiller, S. Marinesco, Electroanalysis 30 (2018) 977–998.
[4] L. Dai, Y. Xue, L. Qu, H.-J. Choi, J.-B. Baek, Chem. Rev. 115 (2015) 4823–4892.
[5] D.J. Lee, J.S. Chang, J.Y. Lai, Bioresour. Technol. 198 (2015) 891–895.
[6] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Appl. Catal. B Environ. 202 (2017) 217–261.
[7] E. Mousset, N. Oturan, M.A. Oturan, Appl. Catal. B Environ. 226 (2018) 135–146.
[8] E. Mousset, S. Pontvianne, M.-N. Pons, Chemosphere 201 (2018) 6–12.
[9] C.A. Martínez-Huitle, M.A. Rodrigo, I. Sirés, O. Scialdone, Chem. Rev. 115 (2015) 13362–13407.
[10] F. Cœuret, J. Appl. Electrochem. 23 (1993) 853–855.
[11] A.J. Bard, L.R. Faulkner, Electrochemical Methods – Fundamentals and Applications, second ed., John Wiley & Sons Inc., New York, 2001.
[12] C.L. Mantell, Electrochemical Engineering, Mc Graw-Hill, New York, 1960.
[13] F. Coeuret, A. Storck, Eléments de Génie Electrochimique, first ed., Tec & Doc, Paris, 1984.
[14] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, first ed., Chapman and Hall, London, 1982.
[15] E. Mousset, A. Diamand, Tech. l’Ingénieur J 3952 (2019) 1–17.
[16] F. Goodridge, K. Scott, Electrochemical Process Engineering: A Guide to the Design of Electrolytic Plant, first ed., Springer, New York, 1995.
[17] E.M. Stuve, Electrochemical Reactor Design and Configurations, in: G. Kreysa, K. Ota, R.F. Savinell (Eds.), Encyclopedia of Applied Electrochemistry, Springer, New York, 2014, pp. 568–578.
[18] F. Walsh, G. Reade, Analyst 119 (1994) 797–803.
[19] F. Coeuret, Ingénierie des Procédés Electrochimiques, Ellipses, Paris, 2003.
[20] F. Dalton, Electrochem. Soc. Interface 25 (2016) 50–59.
[21] F.C. Walsh, G. Kear, A.H. Nahlé, J.A. Wharton, L.F. Arenas, Corros. Sci. 123 (2017) 1–20.
[22] S. Langlois, J.O. Nanzer, F. Coeuret, J. Appl. Electrochem. 19 (1989) 736–743.
[23] A.T. Hubbard, F.C. Anson, Anal. Chem. 38 (1966) 1887–1893.
[24] C. Zhang, S.M. Park, Anal. Chem. 60 (1988) 1639–1642.
[25] O. Scialdone, C. Guarisco, A. Galia, G. Filardo, G. Silvestri, C. Amatore, C. Sella, L. Thouin, J. Electroanal. Chem. 638 (2010) 293–296.
[26] E. Mousset, Y. Pechaud, N. Oturan, M.A. Oturan, Appl. Catal. B Environ. 240 (2019) 102–111.
[27] P. Cognart, F. Bouquet, M. Roustan, Tech. l’Ingénieur J 3804 (2015) 1–14.
[28] E. Mousset, M. Puce, M.-N. Pons, ChemElectroChem 6 (2019) 2908–2916.