Sonoelectrochemistry: Both a Tool for Investigating Mechanisms and for Accelerating Processes

by Jean-Yves Hihn, Marie-Laure Doche, Loic Hallez, Abdeslam Et Taouil and Bruno G. Pollet

Abstract: Surface irradiation by power ultrasound has proven to offer beneficial effects not only for surface cleaning, but also for the modification of functional properties of metallic or organic coatings. However, the process scale-up has failed to match laboratory observations and data, in particular for the design of industrial sono-reactor systems. To solve this problem, electrochemical systems have been developed and used as effective sensors for ultrasonic activity allowing numerous useful quantitative information to help designing better sono-reactor and process control. Moreover, new types of ultrasonic transducers (e.g., focalised ultrasonic transducers) and new progress in the modulation of ultrasonic transducer excitation have pave the way to industrialization.

Keywords : *sonoelectrochemistry – metallic coatings – organic coatings– sonoreactors*

Surface Treatment and Surface Coating

The process of irradiating surfaces with power ultrasound is now widespread, especially in industrial cleaning operations. The principle is very simple: the ultrasonic transducers, vibrating between 20 kHz and up to 400 kHz, are fixed on a tank wall which can contain up to several hundred litres of a solution, in which the ultrasonic wave propagates. In addition to the convective flow generated by the ultrasonic wave absorption, cavitation is induced by the local variation of pressure in the liquid and acts on the contaminants adhering to the metal, plastic,

glass, etc. Millions of very tiny bubbles (1µm to 100µm), perfectly distributed in the liquid, grow before collapsing violently, penetrating in every crevice of the parts requiring cleaning, detaching the stains in a matter of a few seconds.

It is therefore natural to extend this process to the coating process itself, thanks to the increase in mass transfer, due to the agitation induced by convection and cavitation bubble collapse. Moreover, if the bubble collapse occurs in close vicinity of the surface, the surface may either (i) be affected by the ultrasonic shock waves and thus undergo important mechanical effects or (ii) cause a deformation of the bubble and therefore the collapse becomes asymmetric [1]. It is interesting to note that the electronic transfer can also be strongly affected by ultrasound, in turns keeping the substrate surface continuously clean by preventing the formation of 'parasite' layers able to inhibit important reactions [2]. Moreover, the numerous bubbles collapsing at the surface may act as nucleation sites that influence directly nucleation mechanisms, resulting in more random growth [3]. Walker *et al*. [4] were the first to report the benefits of ultrasonic irradiation for metallic coating elaboration. Prasad *et al.* [5]. showed evidence that several properties may be greatly modified and improved, such as brightness and hardness, better adhesion to substrates, finer grains, a reduced porosity and less internal stress.

The use of ultrasound has also been extended to electroless coating on non-conductive substrates, as for example copper deposition on epoxy resins under high frequency ultrasound [6]. Ultrasound not only leads to a considerable increase in the deposition rate, but also in the adhesion (up to 4 N with an increase of almost 40%), whereas the internal stress decreased drastically (down to 50% of the value measured in the coatings obtained under *silent* conditions). The study of corrosion phenomenon in the presence of ultrasound is an 'old challenge', with the main objective of minimizing the synergetic effect termed *corrosion-cavitation* frequently observed at industrial scale for fluid circulation (e.g., tube walls, turbine or pump blades, etc.) or on ships' propellers [7]. Various research studies on a large number of

substrates (e.g., copper alloys, aluminum, stainless steels, etc.) give strong evidence that ultrasound may increase many types of corrosion. Finally, these results have led to the creation of an international standard (ASTM G32-10 [6]) allowing the prediction of metals' behavior in such environments.

A Need for Cavitation Activity Quantification and Characterization

Although power ultrasound offers many advantages at laboratory scale, and thus has attracted a lot of interest since the mid-1990's, only a few cases of 'technology transfer' have taken place in industry. This limited translation to practice is due to the lack of fundamental knowledge and data related to ultrasonic systems' operations. As the intensity of cavitation bubble production modifies drastically the ultrasonic wave propagation and absorption, non-linearity behavior occurs, which in turns prevents the use of simple mechanical laws for accurate reactor modeling.

However, it is possible to use electrochemistry as a tool to study phenomena occurring at an electrode surface and at a given location in a sono-reactor. From a process accelerated by ultrasound, electrochemistry becomes a useful tool to quantify the ultrasonic energy scattered at the immediate electrode surface vicinity. The *electro-diffusional* method will be of great help, consisting in the measurement of limiting currents during linear sweep voltammetry with quasi-reversible redox couples such as Fe^{2+}/Fe^{3+} at low active species concentration in solution. This approach has turned out to be extremely efficient for the determination of acoustic intensity at different locations in the sono-reactor [8]. By systematically moving an electrode in an ultrasonic field, it is possible to map the acoustic activity, especially the zone close to the transducer where the most intense cavitation activity takes place. Then, to demonstrate the 'portability' of our results, i.e., to allow relevant comparisons between experiments performed with different ultrasonic and electrochemical equipment, we proposed to convert the raw

electrochemical values into equivalent velocities *U*, corresponding to normal flows directed toward the electrode surface resulting in the same electrochemical signal than in the presence of ultrasound [9]. Subsequent use of the so-called *Pollet-Hihn* equation [9], makes it possible to obtain a physical quantity characteristic of the ultrasonic activity at each measured point.

***Pollet-Hihn* equation**

$$U = \frac{1}{\left(0.45 \times n \times F \times C^*\right)^2} \times D^{-4/3} \times \upsilon^{1/3} \times r \times j_{\lim}^2$$

where n is the number of electrons transferred, F is the Faraday constant (C.mol^{-1}), C^* is the bulk concentration of the electroanalyte (mol.m^{-3}), D is the diffusion coefficient of the electronalyte (m^2.s^{-1}), υ is the kinematic viscosity (m^2.s^{-1}), r is the electrode radius (m), and j_{lim} is the limiting current density (A.m^{-2})

Comparisons with 'real fluid motion' at a given location becomes possible thanks to Particle Image Velocimetry (PIV) technique (measurement using a high-speed camera and a chemical tracer, allowing tracing the displacement into a 2*D* laser sheet of light). The systematic comparison allows separation of the respective contributions of cavitation events occurring at the electrode surface to the convection flow called *ultrasonic wind* [10].

The main result is that the range of magnitude of the 'real fluid motion' at 20 kHz is about 10 times lower than the calculated equivalent flow. This finding clearly indicates that the main contributor to the extremely high agitation at the sonicated electrode surface is ca. 90% due to cavitation bubble collapse (inc. shock waves as well as microjets). A systematic experimental study was gathered together in a *phenomenological* model and in correlations linking

dimensionless *Sherwood* (representative of agitation) to *Reynolds* numbers (representing flow) and *Schmidt* number (representative of the solution electrochemical properties [1]).

This need for characterization was extended to unconventional solvents such as Room Temperature Ionic Liquids. These solutions present physical and chemical properties particularly interesting for numerous applications in electrochemistry (e.g., actinides separation, electrodeposition of metals, etc.) [11]. Their high viscosities are definitively problematic, but their detrimental effects may be counterbalanced by the strong agitation provided by ultrasound. Thus, the study of the behavior of redox couples adapted to this type of solvents have been undertaken in a micro-sono-reactor designed for this purpose [12] (Figure 2). Depending upon the solvent nature, it was found that the limiting current density (j) decreased in the following order: CH_3CN, water, [Bmim] [Tf_2N], in good agreement with the variations observed for the electroactive species diffusion coefficient (D). However, while regrouping the electrochemical measurements in Sherwood dimensionless criteria, a single behavior of the [Bmim] [Tf_2N] was observed. At similar ultrasonic intensity transmitted to the media (1 $W.cm^{-2}$), ultrasonic agitation was found to be more efficient in ionic liquids comparatively to water or acetonitrile. Then, the sonoelectrochemical responses of the redox couples in four ionic liquids ([Bmim] [Tf_2N], [Omim] [Tf_2N], [N1113] [Tf_2N] and [Bmpyr] [Tf_2N]) as well as in various mixtures of given viscosities (water/PEG, acetonitrile/PEG and acetonitrile/[Omim] [Tf_2N]) were generated and were compared to those obtained under *silent* conditions at a rotating disc electrode (ω = 5,000 rpm). The data showed that there were two groups of solvents behaving distinctively under sonication: one group for which the interaction 'ultrasonic wave/electrolyte' was comparable to that of water only, and another one for which the liquid structuration was different, translated by an eight-fold increase in mass-transfer under ultrasonic conditions [13].

This control of the ultrasonic parameters was found to be a major milestone for the design of sono-reactors and their applications. For example, the determination of an "equivalent" tangential equivalent flow was crucial in the design of boats hull cleaning tools (Navy Clean company [14]). The intense activity of ultrasound on a surface can be used to develop and implement accelerated corrosion tests and to obtain faster responses to corrosion protection level of coatings while complying with the natural corrosion mechanisms and therefore remaining close to natural conditions. Examples of such an application of ultrasound include studies of zinc-coated steels under different electrolytes with the view of reproducing atmospheric conditions [15] or on stainless steels [16]. For example, the rate of corrosion in 0.5 M Na_2SO_4 electrolyte is directly proportional to the distribution of the cavitation activity in the sono-reactor (Figure 3 (a,b)). The figure shows agitation maxima, the positions of which depend upon the ultrasonic frequency and the distance between the electrode and the ultrasonic horn in a 'face-to-face' configuration. The position that increases uniform corrosion the most was at a *sample-ultrasonic horn* distance directly proportional to the quarter of a wavelength, $\lambda/4$. By modifying the ultrasonic frequency and the signal amplitude, it becomes possible to modulate the corrosion 'intensity'. Alternatively, ultrasound pulses can induce a *switch on/switch off* effect, corresponding to passivation/depassivation conditions of the 304L stainless steel in sulfuric acid enriched in chlorides [17]. In addition, ultrasound has been shown to greatly accelerate the pitting corrosion generated in halide media [16].

The use of sonoelectrochemistry in 'anodic mode' is very rare for metal treatment, but an increasing number of studies have been carried out in electropolymerisation processes [18]. Cavitation bubble collapse seems to be at the origin of a better distribution of nuclei at the surface, and a better solubility of the monomers under ultrasound [18]. Thus, coatings with a finer and more homogeneous topography can be obtained as shown in Figure 4, allowing a high number of applications possibilities where the surface morphology plays a key role (e.g.,

sensors, corrosion protection etc.) [18]. Films formed under irradiation are much more compact in texture leading to a reduced mobility of the ions within the films, and the possibility of controlling the movement of the charged species within the organic matrix. It should be noted that the electrical conductivity of organic coatings is slightly reduced under sonication, due to the partial degradation of the polymer chains [19]. For example, the conductivity of perchlorate-doped polypyrrole was found to decrease from $0.3 \times 10_4$ to $0.2 \times 10_4$ S/m. That said, a selective modification of the surface at a strictly delimited zone becomes is also possible with High Intensity Focused Ultrasound (HIFU) transducers, which possess a concave emitting surface that allows the focusing of the high frequency acoustic wave over an area of a few mm_2 [20]. The acoustic intensity generated by this type of technology can exceed the performance of flat transducers, reaching several kW/cm^2 with fluid velocity up to 10 cm/s at the focal length. Their integration into electrochemical processes was conducted in conjunction with IMASONIC company (Figure 5). For polymers layers with acoustic impedance close to that of water, the acoustic energy is converted into heat by viscous friction, at the opposite (i.e., a reflective surface), an ultrasonic standing wave is established and gives rise to a cluster of cavitation bubbles that erode the surface. By optimizing all these parameters in collaboration with C & K Components, a reel-to-reel process was designed for the removal of a masking resin [21, 22], with a view to obtaining selective deposits. The resin deposited on connectors in continuous scrolling was melted and expelled within a few milliseconds from the chosen zone. The band covered with partially ablated resin underwent an electrolytic coating of precious metals which was selectively deposited on the areas denuded by the HIFU. Finally, this need to control cavitation, i.e., to amplify or completely quench cavitation events, led us to study the frequency modulation of ultrasound [23]. This phenomenon uses the ability for the bubbles to oscillate in resonance with the acoustic wave. For a positive frequency sweep (towards high frequencies), the bubbles become too large to resonate in phase with the ultrasonic wave whereas for a

negative sweep, a larger number of bubbles can be activated depending upon the sweep rate, opening the doors to an effective control of the acoustic activity in a very wide range.

Conclusions

With a good knowledge of the cavitation activity mechanisms and of their specific influence on electrochemical processes, it is possible to define the best conditions of the use of power ultrasound in many applications, from accelerated corrosion to cleaning and coating elaboration. This is of considerable importance, by considering both favorable added value/energetic cost ratio and scale-up ability of sonoelectrochemical systems.

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Figure 1: Example of a flow velocity vector field in a sono-reactor, close to an electrode

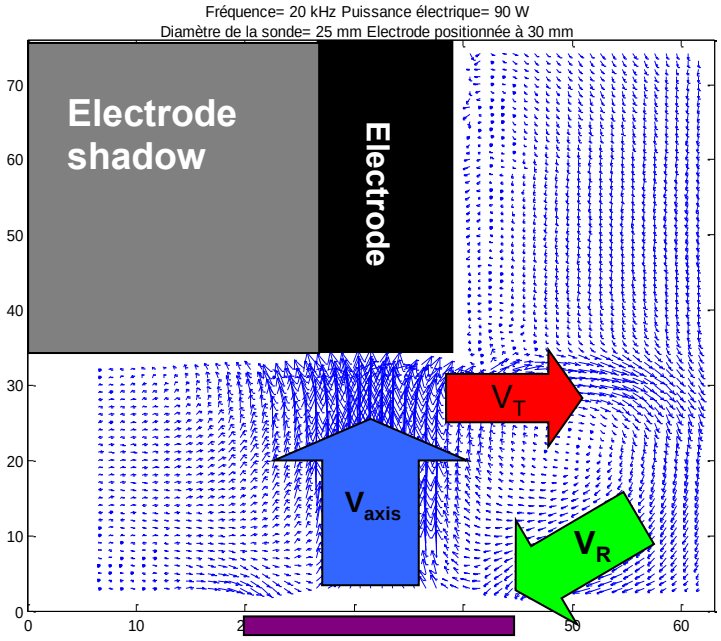
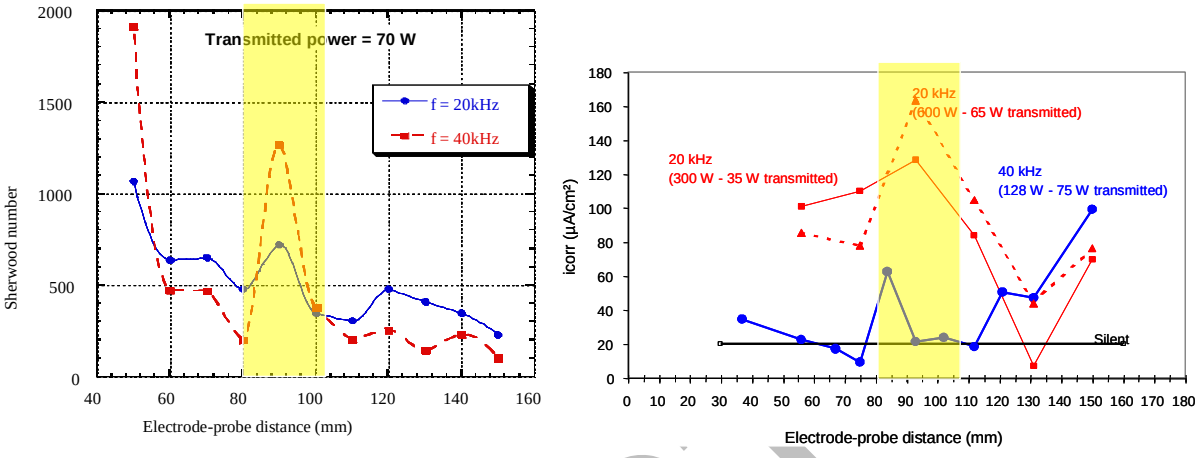


Figure 2 – Sono-reactor set up for the electrochemical measurements with RTIL's

Figure 3 - (a) Variation of the mass transfer in a corrosion cell under sonication from 20 kHz and 40 kHz and various horn to electrode distances; (b) Corrosion rates of zinc coated steel plates measured in the same conditions



(a) **(b)**

Figure 4 - Characterization of surface morphology by AFM, SEM and optical microscopy of conducting polymer films elaborated under *silent* and high frequency ultrasonic conditions

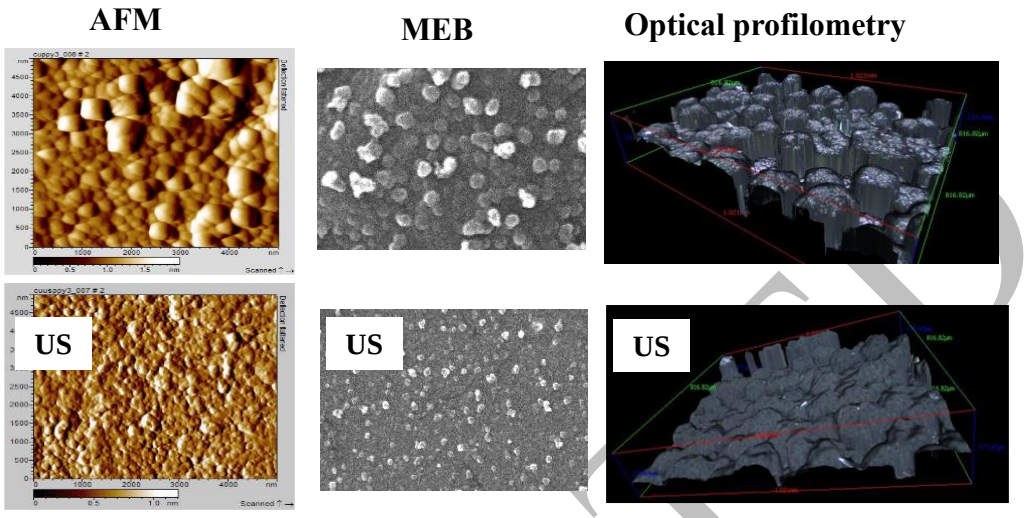


Figure 5 – Ultrasonic irradiation of a metallic target by HIFU

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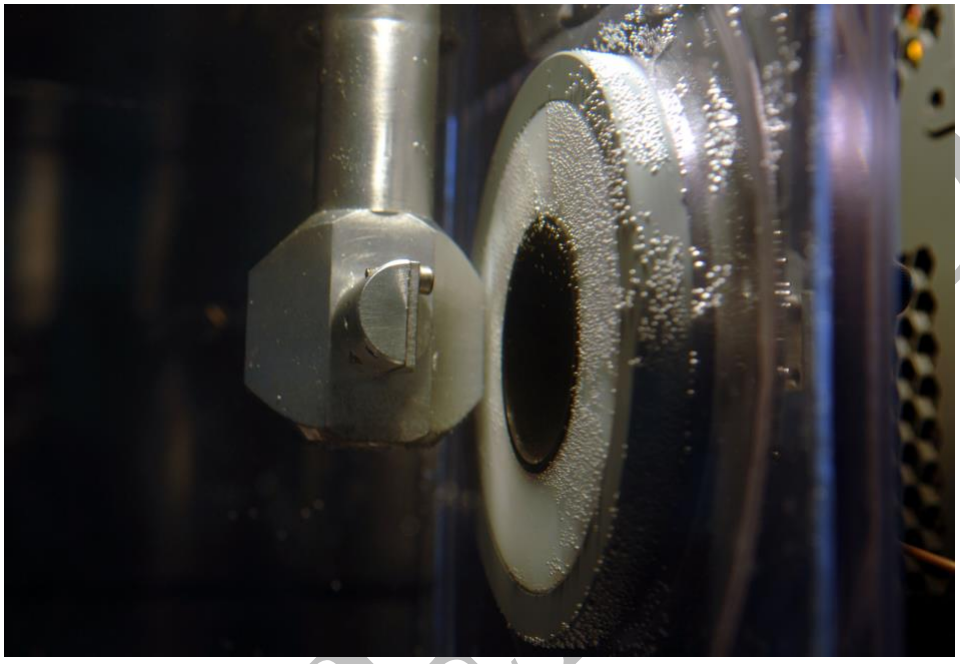

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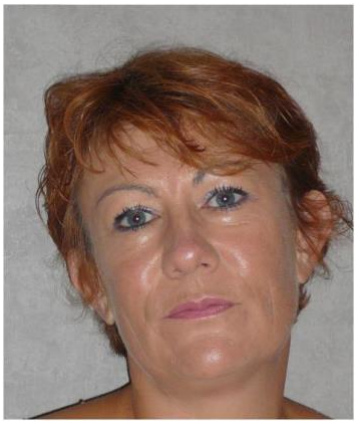

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