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1 Probing water uptake gradient in an epoxy matrix via 2 scanning electrochemical microscopy

3 A. Renaud¹, F. Hache², Y. Elkebir¹, J. Valette³, S. Mallarino¹, D. Trinh¹, S. Touzain¹

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5 1 : Laboratoire des Sciences de l'Ingénieur pour l'Environnement (LaSIE) UMR CNRS 7356, Université
6 de La Rochelle, Pôle Sciences et Technologie, Avenue Michel Crépeau, 17042 La Rochelle Cedex 1,
7 France

8 quang-dao.trinh@univ-lr.fr

9 2 : Institut Ingénierie Mécanique (I2M), CNRS Université de Bordeaux, 15 rue de Naudet, 33170
10 Gradignan, France

11 3 : TENSYL, 48 rue Jacques de Vaucanson, Pôle Arts et Métiers, 17180 Périgny, France
12

13 Abstract

14 Scanning electrochemical microscopy (SECM) is used to detect and observe the presence of water
15 inside polymeric film at the microscopic scale around 200-500 μm . The principle is based on the use
16 of SECM performed with a room temperature ionic liquid (RTIL) and $\text{K}_4\text{Fe}(\text{CN})_6$ as redox sensor. The
17 particular electrochemical behaviors obtained in such medium have been investigated by performing
18 cyclic voltammetry and approach curves in negative feedback mode. Then, the cross-section of epoxy
19 resin films has been repeatedly scanned using the SECM probe over several days of immersion in the
20 RTIL. As the presence of water impacts the electrolyte viscosity, the electrochemical signal was
21 sensitive to the amount of water around the microelectrode. The sensitivity of this technique to the
22 presence of water released from the materials at the microscopic scale was demonstrated by
23 comparing electrochemical signals obtained on dry and saturated specimens. Such results appeared
24 to be very promising for the development of new methods to locally detect the presence of water in
25 thick polymeric materials and to measure humidity gradient within the material thickness.

27 Keywords

28 Room temperature ionic liquids (RTIL); Scanning electrochemical microscopy; SECM; Water
29 detection; Epoxy resin

30

31 **1. Introduction**

32 Among the various environments to which human technologies can be exposed, immersion in fresh
33 water is one of the harshest conditions. In particular, metallic components can be subjected to strong
34 corrosion phenomena and then lead to the failure of structural parts [1–3]. For this reason, polymeric
35 materials are often preferred for immersed applications and are widely used in marine and
36 submarine environments [4–6]. Parts can be made of pure polymeric materials (thermoplastic or
37 thermoset matrixes) or various composite structures, such as glass fiber reinforced polymers (GFRP)
38 or carbon fiber reinforced polymers (CFRP) [7–9]. Even though these lasts are not subjected to
39 corrosion processes, they can still interact with the surrounding aqueous environment [10–12]. In
40 particular, water molecules can penetrate and diffuse to the bulk of the immersed parts. The amount
41 of absorbed water and the kinetics of the water ingress strongly depend on the chemical nature of
42 the polymeric matrix [13]. Other internal parameters (manufacturing process, microstructure) or
43 external parameters (temperature and composition of the aqueous environment) can also impact
44 the quantity of water at the equilibrium and the speed of the water penetration [14].

45 In the case of thin polymeric systems, such as layers or membranes, the water saturation state is
46 quickly reached and the specimens behave as homogeneous hydrated materials [15]. However,
47 thicker parts need much more time to attain equilibrium [16], leading to the presence of a long-term
48 humidity gradient through the thickness of the specimens. For instance, blades of industrial turbines
49 are usually made of sandwich composites with glass/epoxy skins whose thickness vary from few
50 millimeters at the tip up to few centimeters at the base. Thus, the time needed to reach a
51 homogeneous water saturation state can be very long and the parts can present humidity gradients
52 for the major part of their service life. Obviously, such gradients induce a heterogeneous distribution
53 of properties (mechanical, dielectric, etc.) through the thickness of the materials. In such case, the
54 modeling and the prediction of the macroscopic behavior of the whole parts becomes imprecise and
55 much more complex. Being able to access the humidity gradient through a specimen is then a key
56 step in predicting and understanding its global properties. Indeed, the durability of those blades is
57 critical for the expected turbine life of 10 to 20 years. The prediction of the humidity profile, of the
58 fatigue state and of the coupling of these processes is a primary interest. Therefore, the evaluation of
59 the water distribution through the laminates has to be addressed.

60 Even though diffusion laws such as Fick [17,18] or Langmuir equations [19,20] are very useful for the
61 prediction of water concentration in a material, it becomes more difficult to use them for
62 heterogeneous materials or structures with complex geometries. If the diffusion parameters

63 describing the water uptake kinetics and equilibrium are not well known and characterized, the
64 challenge gets even bigger. A large number of studies deal with the estimation and the prediction of
65 such profiles [21–25].

66 If one wishes to know the distribution of water involved in a solid material, IR and Raman
67 microscopes give precise information in a short time. The concentration of water vapor can be
68 detected by the optical hygrometer measurement. The first known measurements of the water
69 vapor absorption in the infrared (IR) were performed by Fowle (1912) [26]. There are some
70 important requirements for the selected wavelength: minimize the collision broadening with the
71 other components, high selectivity with regard to water, and high contrast in optical properties
72 between water and other components of the material [27].

73 There are some drawbacks when using the IR, or Raman microscopies to evaluate the water content
74 in epoxy resin. Andrey E. Krauklis et al. [28] used the Fourier transform near-infrared (FT-NIR)
75 spectroscopy to measure the water content of amine-epoxy neat resin and Fiber-Reinforced
76 Composites. Based on the physics of Beer–Lambert law, this method can be used to a wide range of
77 samples, including thin ones. However, it is important to keep in mind that this approach has some
78 drawbacks. As an example, monitoring of carbon fiber-composite materials is likely to be limited if
79 the sample is too thick or non-transparent within the researched radiation wavelength range. Other
80 spectroscopic approaches include Raman, which is less sensitive to water than FTIR, and reflectance
81 FTIR, which primarily provides information on the material's surface. The weak sensitivity of water
82 detection is a downside of Raman spectroscopy. The conversion efficiency of the Raman effect is low
83 because only a small fraction (approximately 10^{-6}) of the original photons are non-elastically
84 dispersed [29].

85 C. Marro Bellot et al. [30] have embedded evanescent optical fiber sensors at different depths of a
86 composite material to detect the moisture diffusion through the thickness of the epoxy samples.
87 Eight sensors were used at depths ranging from 0.8 to 2.3 mm. Since the number of the sensors are
88 limited, the resolution of this method is weak and not applicable to study the water profile of a thin
89 epoxy resin (thickness around 400 μm).

90 The SECM technique could be fruitful to measure the moisture profile of the epoxy material. Using
91 the electrochemical scanning tip with a diameter of 10 μm , water molecules can be locally detected
92 by the current of the tip so the humidity profile can be estimated. Instead of using several embedded
93 sensors, this method relies on the electrochemical scanning tip, which can measure smaller
94 dimension, with a higher scanning resolution. This method can also be applied to a transparent or
95 non-transparent sample because the measured signal is the electrochemical current.

96

97 This work focuses on the detection of the water profile across the material thickness by using
98 scanning electrochemical microscopy (SECM) experiments performed in a dry room temperature
99 ionic liquid (RTIL). After a theoretical justification of the proposed methodology, the experimental
100 protocol is detailed and first results are presented, validating the consistency of the method.

101 **2. Principle**

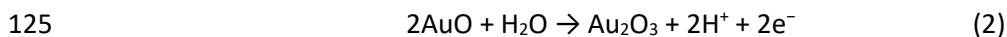
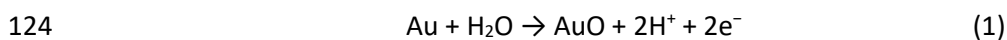
102 **2.1. Detection of humidity in RTILs using electrochemistry**

103 The SECM technique has already been used on polymeric materials in order to investigate various
104 phenomena such as dimensional swelling [31], physical aging [32] or internal stress [33]. In these
105 studies, electrochemical measurements have been performed in aqueous electrolytes [34,35] in
106 order to perform an in-situ monitoring of the swelling when the specimens were exposed to water.

107 In the case of the present work, the approach is quite different. Naturally, trying to detect the
108 presence of water via an aqueous media would be a nonsense. Nevertheless, electrochemistry can
109 also be performed in several non-aqueous electrolytes. For instance, RTIL have been widely
110 developed in the past years to perform original electrochemical reactions [36–40]. Nkuku et al. [41]
111 have demonstrated the feasibility of performing SECM with ferrocene dissolved in non-aqueous
112 solvent (deep eutectic solvent). However, the high viscosity of the solvent leads to specific behaviors
113 due to convection and diffusion mixed regimes. In such a high viscous solvent, the diffusion
114 coefficient of redox species in RTIL are a hundred times lower than those in aqueous media [42].
115 RTILs can also be used to analyze the inward and outward electrolyte diffusion processes (in dry
116 conditions) in epoxy coatings [43].

117 In the presented method, a water-free RTIL is used as electrolyte in order to detect water molecules
118 coming from a wet thermoset material sample. Indeed, the impact of the presence of water on
119 electrochemical signals obtained in RTILs has already been demonstrated by different authors. Two
120 main cases can be distinguished.

121 Redox activity provided by water molecules: Zhao et al. [44] performed voltammetry experiments
122 using a gold electrode in two aprotic RTILs containing different amounts of humidity. Water
123 molecules are involved in the following reactions (Eqs. (1) and (2)):



126 The voltammetry signal, and more specifically the current peak associated with Eq. (1), is significantly
127 impacted by the amount of water present in both tested RTILs. The authors also demonstrated the
128 linear relation between the water concentration in the RTILs and the current peak value.

129 Redox activity provided by an additional compound: Qian et al. [45] performed cyclic voltammetry
130 and square wave voltammetry in RTILs using potassium ferricyanide as the redox specie. Even though
131 water is not involved in the electrochemical reactions observed by voltammetry, a linear relationship
132 between the amount of water in the RTILs and the anodic peak current measured in square wave
133 voltammetry has also been emphasized. The linearity has been observed in both hydrophilic and
134 hydrophobic RTILs. The authors demonstrated that the dependence between the water
135 concentration and the anodic peak current in the bulk solution can be attributed to the impact of
136 water molecules on the viscosity of the RTIL and then on the diffusion coefficient of the redox specie.
137 Indeed, the anodic peak current value of a macroscopic electrode can be approximated by the
138 Randles-Sevcik equation (eq 3) [46]:

$$139 \quad i_{peak} = 0.446nFAC_0 \left(\frac{NF}{RT}\right)^{1/2} v^{1/2}D \quad (3)$$

140 where n is the number of electrons transferred per molecule, F the Faraday constant, A the area of
141 the electrode, C_0 the concentration of the redox probe, v the scan rate and D the diffusion
142 coefficient. This diffusion coefficient of the redox species depends on the viscosity of the RTIL, which
143 is itself dependent on the presence of water molecules. It is worth to mentioning that Qian et al. [47]
144 also checked that the presence of potassium ferricyanide does not affect the diffusion of water in the
145 RTILs.

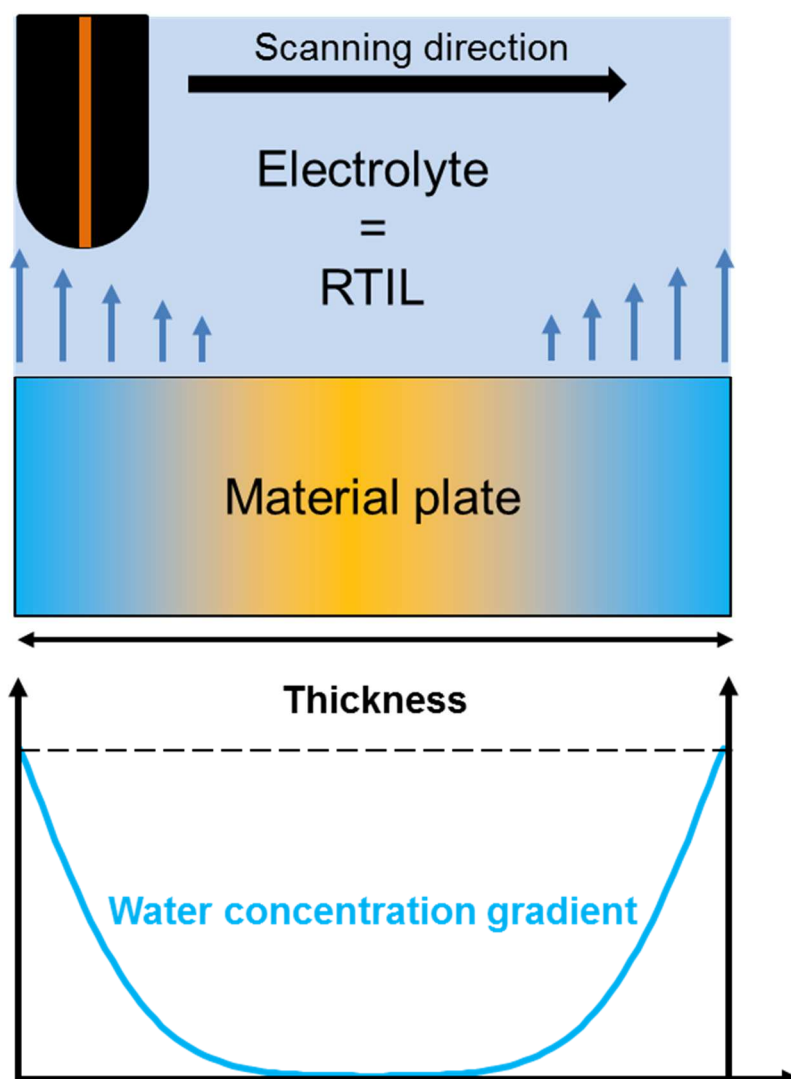
146

147 **2.2. Electrochemistry in RTILs brought to the microscopic scale**

148 The tight relation between the amount of water in a RTIL and the electrochemical response has been
149 demonstrated on macroscopic electrodes. The purpose of the present work is to apply this principle
150 at the local microscopic scale, using a microelectrode. The SECM technique has been greatly
151 developed in the past decades and finds relevant applications in a broad range of research fields
152 [31,48–51]. This scanning technique allows investigating local electrochemical reactions at the
153 microscopic scale. In this paper, SECM is performed in a RTIL using the principle previously detailed in
154 order to locally assess the presence of water. This approach takes advantage of i) the low diffusivity
155 of water molecules in the RTIL, ii) the RTIL hydrophilicity to force the water to get out of the material,
156 iii) the water-free environment that prevents to have experimental artifacts and iiiii) the use of

157 microelectrodes to measure the local concentration of the redox mediator close to the polymeric
158 material.

159 Figure 1 illustrates the developed protocol. A microelectrode (10 μm diameter) is used as the SECM
160 tip. The SECM tip is scanned over the polymeric material, with a constant tip-to-sample distance of 5
161 μm . The polymeric material plate, that was previously immersed in water, presents a humidity
162 gradient through its thickness. Depending on the hydrophilicity of the RTIL and on its viscosity, water
163 molecules will progressively come out of the polymeric material and diffuse within the RTIL, locally
164 modifying the electrochemical properties of the electrolyte, especially the current intensity. The
165 variations of the electrochemical signal over a scan line can then be attributed to the local
166 concentration of water in the RTIL, which is itself depending on the local amount of water in the
167 material. Obviously, electrochemical variations will be more representative of the humidity gradient
168 as the microelectrode is brought as close as possible to the specimen surface.



169

170 Fig. 1: principle of the local detection of water molecules coming out of a wet specimen with a water
171 concentration gradient through its thickness

172 To electrochemically detect water molecules, potassium ferricyanide $K_4Fe(CN)_6$ has been used as the
173 redox mediator. Because the electrochemical process in this approach does not include water, no
174 water is produced or consumed during the measurement, which eliminates the possibility of
175 artefacts. The choice of the RTIL has been done according to two criteria: hydrophilicity in order to
176 promote the desorption of water from the specimen, and high viscosity in order to have a slow
177 diffusion of water in the RTIL and offer enough time for measurement. For these reasons, 1-butyl-1-
178 methylpyrrolidinium triflate has been selected.

179 As mentioned hereinbefore, due to the high viscosity of RTIL, one should consider the mixed
180 convection-diffusion regime. This term can be characterized by the Peclet number (Pe) [52,53]:

$$181 \quad Pe = \frac{v_{tip} a}{D} \quad (4)$$

182 where v_{tip} the tip velocity, a the tip radius, and D the diffusion coefficient.

183 Moreover, potential unexpected interactions between this RTIL and the resin samples have been
184 previously checked by immersing dry epoxy specimens in the RTIL, for 5 days. No mass variations and
185 no dimensional changes have been observed, attesting the absence of swelling and/or degradation
186 mechanisms when the polymeric materials are exposed to such electrolytes.

187 **3. Sample preparation**

188 **3.1. Specimens**

189 To validate the protocol, samples of epoxy resin have been prepared. They were obtained by mixing
190 an epoxy precursor (diglycidylether of bisphenol A or DGEBA, Sigma Aldrich, ref. 1675-54-3) with an
191 amine hardener (Jeffamine 230, Sigma Aldrich, ref. 9046-10-0).

192 Both components have been mixed using a mechanical mixer for 10 minutes and up to 2500 rpm.
193 The mixture is then degassed for 20 min at room temperature to remove any air bubbles. The resin is
194 then spread between two aluminum plates covered with a sheet of Teflon and spaced by spacers in
195 order to control the thickness of the films (thickness 200 - 500 μm) and cured at 120 °C for 14 hours
196 [54]. Such low thicknesses have been chosen in order to obtain samples that can be quickly saturated
197 with water.

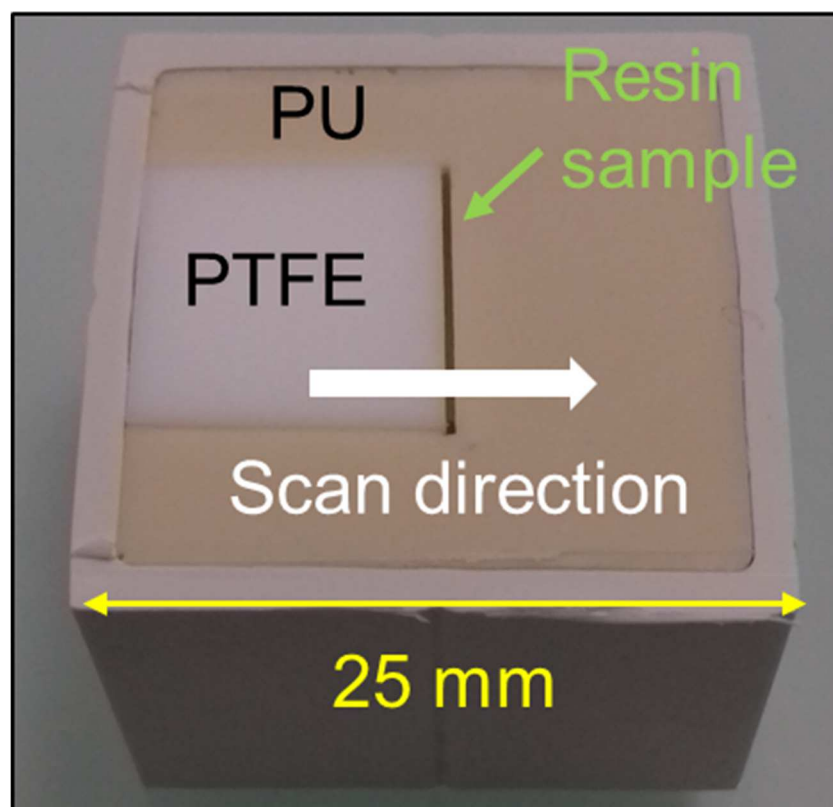
198 **3.2. Conditioning**

199 After elaboration, samples have been dried for at least one week under vacuum in a desiccator to
200 remove any potential water present in the films.

201 To emphasize the ability of the method to locally detect water from a wet material, dry samples have
202 been compared with saturated ones. To reach water saturation, resin specimens have been
203 immersed in distilled water at 35 °C for 5 days and frequently weighted until the water uptake
204 reaches its saturation value of about 3 % in weight.

205 3.3. Testing protocol

206 As the sample has to be fixed during the experiment, a sample holder made of PU resin and PTFE has
207 been built and used after drying, as presented on figure 2. The scanned surface should be as flat as
208 possible in order to avoid topographic artefacts. This means that the sample surface has to be cut
209 and equalized with the surface of the PU and PTFE materials from the sample holder. However,
210 polishing is excluded, with or without water. Indeed, wet polishing would bring unexpected water to
211 the system, and dry polishing would increase the temperature of the sample surface due to friction
212 and induce desorption of water molecules. For the same reason, the duration of the preparation of
213 the sample system should be as short as possible in order to limit water desorption before the
214 analysis.

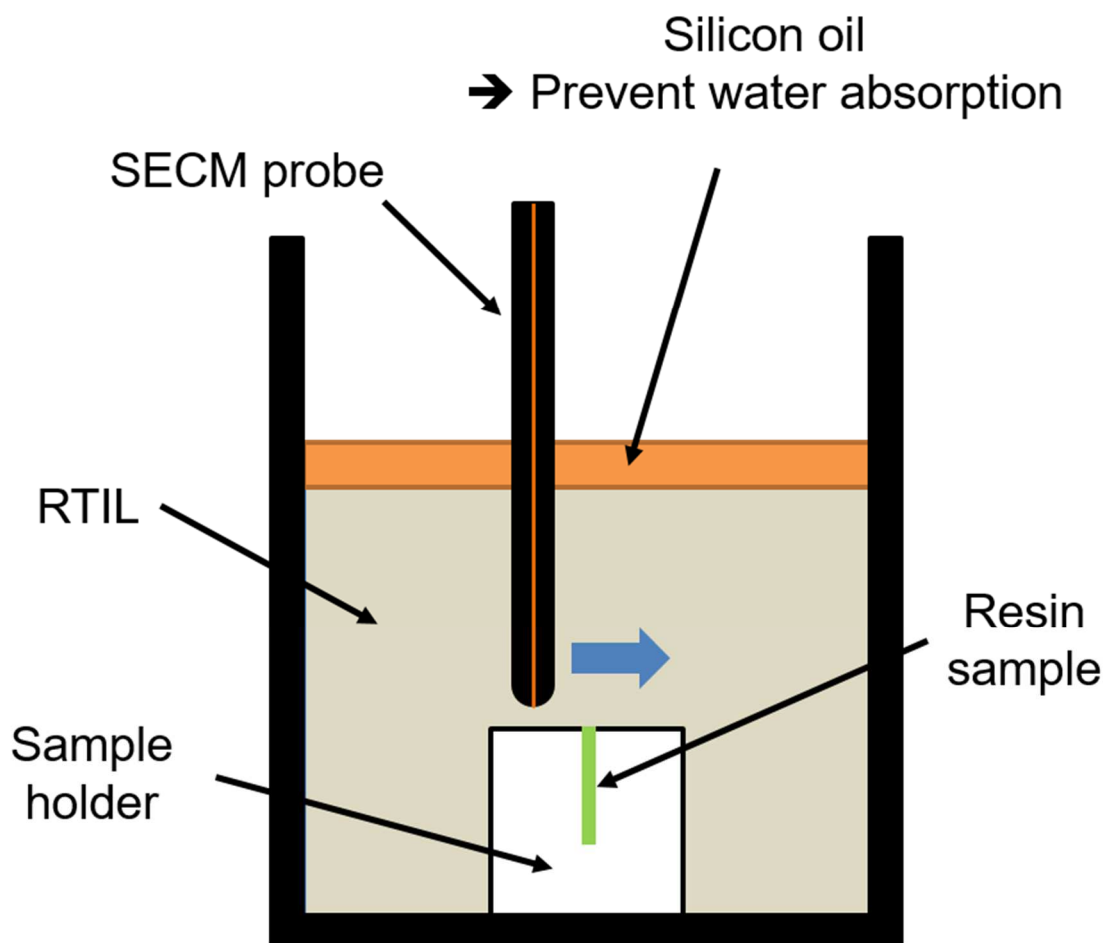


215

216

Fig. 2: sample holding system

217 After extraction from the desiccator or from the immersion bath, resin samples have been directly
218 clamped into the sample holder and the surface has been cut using a microtome knife equipment
219 model HM 340E from Microm Microtech, offering a fast, dry and room temperature cutting process.
220 The sample holding system has then been inserted in the electrochemical cell (figure 3) and the RTIL
221 has been poured to start the experiment. Finally, in order to prevent water ingress from the air, a
222 thin layer of liquid silicon oil has been deposited on top of the RTIL liquid. The proposed setup
223 ensures that the local variations of the electrochemical signal are only attributed to the water coming
224 from the resin sample.



225

226

Fig. 3: Experimental setup during the electrochemical tests

227 The settings of the experiment have been optimized based on the preliminary electrochemical
228 investigation, in order to guarantee a good compromise between the resolution of the
229 characterization and the acquisition of a sufficiently high electrochemical current approach curves. A
230 distance of 5 μm between the microelectrode and the sample has been chosen based on approach
231 curves.

232

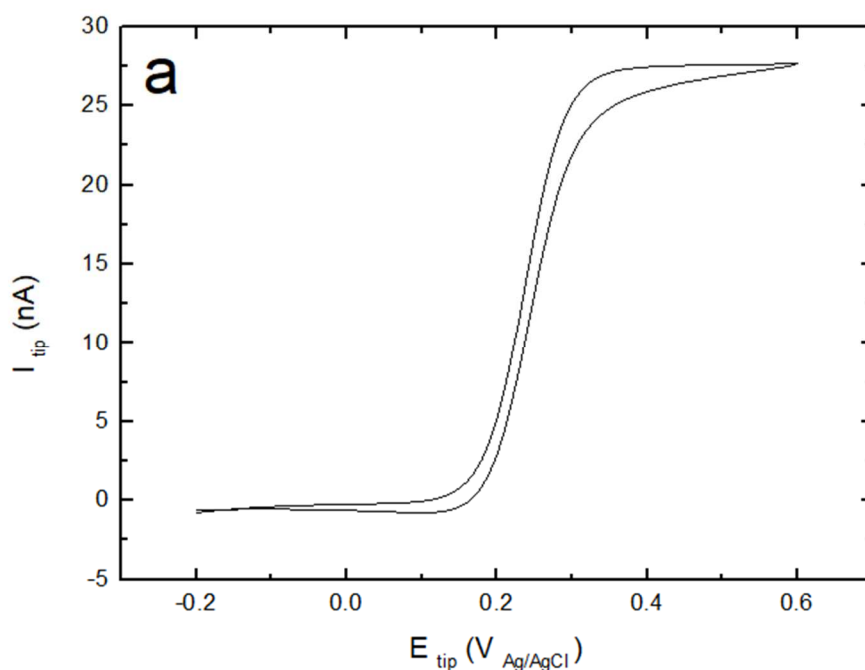
233 **4. Experimental setup**

234 SECM measurements have been performed using a SECM M470 equipment from Biologic, equipped
235 with a platinum microelectrode with a diameter of 10 μm . The counter electrode, which also stands
236 as a pseudo-reference, was a platinum wire dipped into the RTIL. The temperature was controlled by
237 a thermostat cell at 25 $^{\circ}\text{C}$.

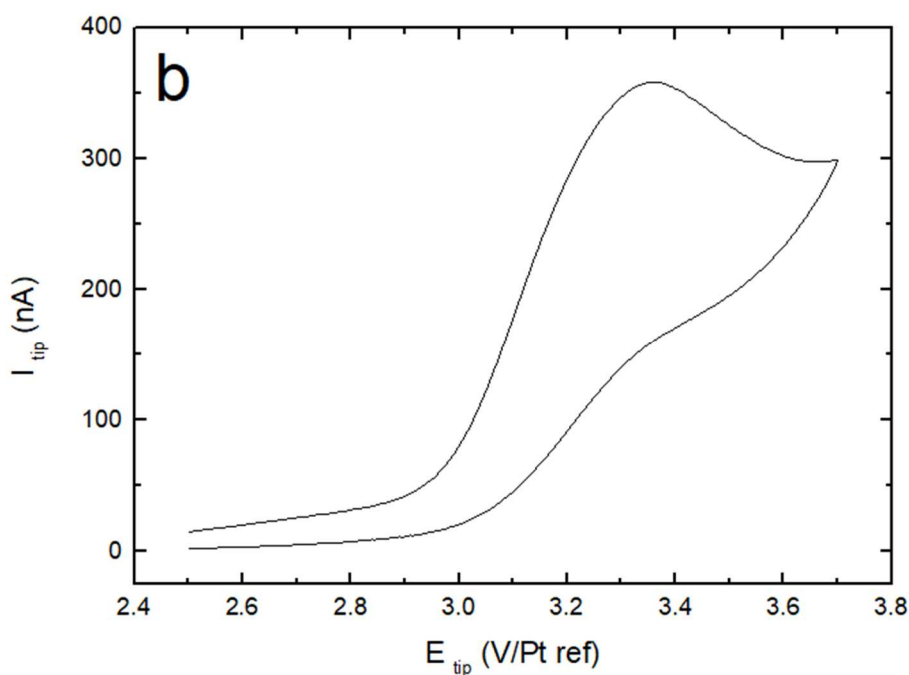
238 Potassium ferricyanide $\text{K}_4\text{Fe}(\text{CN})_6$ was added to the RTIL in order to get a 10 mM concentration and
239 to provide the redox activity. In order to remove any trace of water, the RTIL solution has been dried
240 at 60 $^{\circ}\text{C}$ for at least 90 minutes under vacuum in a desiccator [55]. Then, after cooling down to 25 $^{\circ}\text{C}$,
241 the electrolyte was poured at the very last minute before the beginning of the experiments.

242 Cyclic voltammetry has been performed using this setup in order to verify the electrochemical
243 processes occurring at the microelectrode in the RTIL. Figures 4.a and 4.b present the obtained
244 voltammogram of the $\text{K}_4\text{Fe}(\text{CN})_6$ dissolved in water and in RTIL, respectively.

245



246

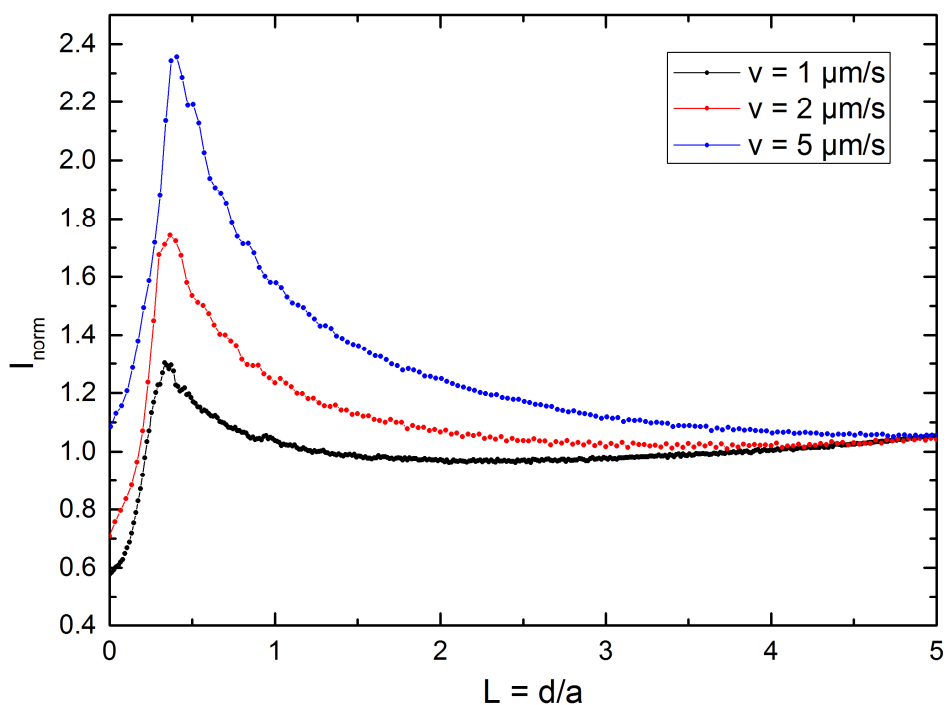


247
 248 Fig. 4: Cyclic voltammogram (sweep rate 20 mV/s) obtained a) in water, and b) in RTIL for the
 249 $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple

250 In these conditions (RTIL + pseudo-reference), the standard potential of the redox couple was
 251 estimated to be approximately $E_0([\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}) = 3.25 \text{ V/Pt ref}$. As mentioned previously, at
 252 the same sweep rate, it is more difficult to obtain the steady state voltammogram at the
 253 microelectrode in RTIL compared to water because of the very slow diffusion of redox species in the
 254 RTIL. Figure 4b shows the non-steady-state behavior of the microelectrode in a high viscous
 255 environment. This behavior has been confirmed by the study of the effect of viscosity on steady-state
 256 voltammetry of the SECM microelectrode by Kevin R. J. Lovelock et al [56].

257
 258 Figure 5 presents the normalized approach curves in the RTIL for 3 approaching speeds $v = 1; 2; \text{ and } 5$
 259 $\mu\text{m/s}$, respectively. It should be noted that $1 \mu\text{m/s}$ is the lowest scan speed allowed by the setup. By
 260 approaching the tip to the insulating material, negative feedback approach curves could be observed.
 261 However, when the tip approaches near the surface ($L = 0.5$), the tip current increases. The shape of
 262 such approach curves can be surprising compared to what is usually obtained in aqueous
 263 electrolytes. Due to the high viscosity of RTIL, the moving microelectrode can induce forced
 264 convection phenomena. Forced convection contributes to the additional flux to the tip, thereby
 265 increases the tip current. This behavior has been observed and explained by C.A. Nkuku et al [32].

266



268

269

Fig. 5: Normalized approach curves obtained in RTIL for different speed values.

270 In particular, the current peak occurring as the tip reaches the surface is specific to viscous media.
 271 This phenomenon has been well described and explained by Nuku et al. [53], linking it with
 272 convection processes at the neighborhood of the surface. The amplitude of this current peak is
 273 directly related to the speed of the microelectrode, as shown on figure 5. This unusual behavior is
 274 also observed in other high viscosity RTILs [57].

275 The Peclet number (Pe) depends on the tip velocity, electrode radius and diffusion coefficient (see
 276 eq. 4). For example, in water, the typical Pe value is 0.03 (with $a = 10 \mu\text{m}$, $D = 7 \times 10^{-10} \text{ m}^2/\text{s}$, $v = 2$
 277 $\mu\text{m/s}$), but in this RTIL, Pe is much higher and equal to 4.44 (with $a = 10 \mu\text{m}$, $D = 4.5 \times 10^{-12} \text{ m}^2/\text{s}$, $v = 2$
 278 $\mu\text{m/s}$). In both cases, the speed values and the tip radius are the same, only the diffusion coefficient
 279 of the redox mediator D changes. Choosing the very slow tip velocity can reduce the Pe value. It can
 280 be observed that this current peak is obtained for all the tested speed values. As $1 \mu\text{m/s}$ is the lowest
 281 approaching speed available on the equipment, this unusual behavior cannot be avoided with the
 282 experimental setup used in this work.

283 The approach curves (Fig. 5) present a current plateau far from the surface, and a sharp current drop
 284 as the microelectrode arrives on the surface, which is typical for an approach curve performed on an
 285 insulating material. Indeed, the proximity between the sample surface and the microelectrode blocks

286 the arrival of redox species, drastically diminishing the current value. Approach curves can then be
287 used in the negative feedback mode to find the position of the specimen surface.

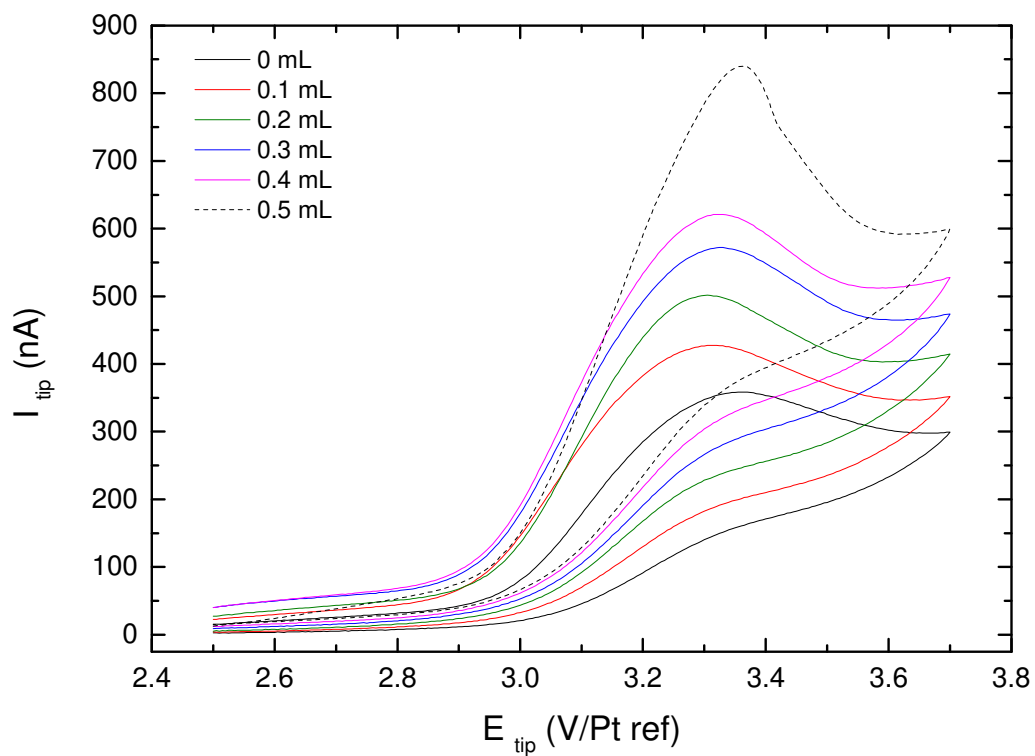
288 During this work, the approaching speed is fixed as 2 $\mu\text{m/s}$ in all measurements (approach curves,
289 and scan lines). This speed has been chosen as a compromise between the limitation of convection
290 phenomena and the scan duration.

291 In order to get as close as possible to the surface of the specimens, approach curves have been
292 performed to detect the position of the specimens. The tip is then retracted from the material
293 surface of about 5 μm . Repeated scan lines have then been performed above the material surface at
294 this same tip-to-substrate distance.

295 The SECM tip can be used to detect the amount of water released from the material. A simple test is
296 made to verify this approach: a small amount of water is added in the ionic liquid, and the tip current
297 is measured for each addition. At the end, 1 ml of water was added to 45 ml of ionic liquid, so the
298 concentration is 0.025 ml of water per 1 ml of RTIL. Before measuring the tip current, the mixture is
299 well homogenized for 5 minutes.

300 Figure 6 shows the cyclic voltammetry results during the addition of water. The tip current increases
301 with the amount of water present in the RTIL because the diffusion coefficient increases as the
302 volume of water in RTIL grows, as previously explained. This result demonstrates that this method
303 may be used to detect and measure the humidity gradient emitted by an epoxy substance.

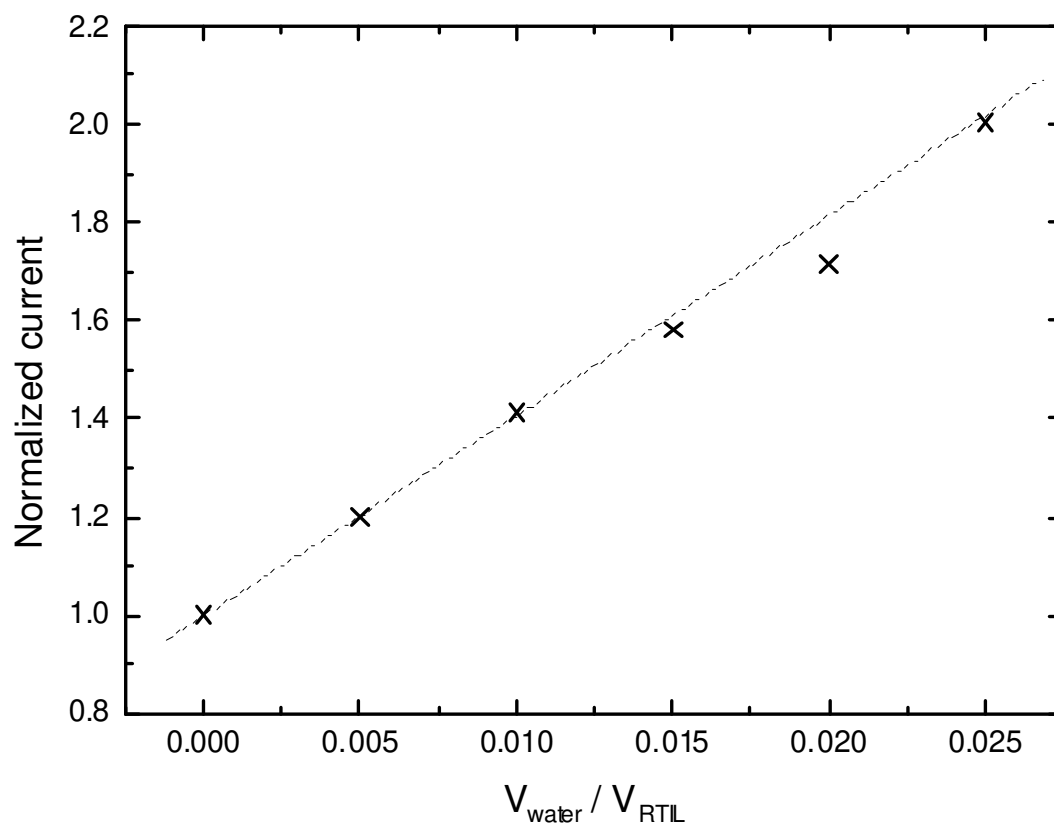
304



305

306 Fig. 6: Cyclic voltammetry of the tip obtained for different water volume added into the dry RTIL

307 A calibration curve can be used to quantify the water content released from the material. Figure 7
 308 presents the calibration curve of the normalized current of the tip as a function of the humidity
 309 amount in the bulk solution (the ratio between the water volume added over the ionic liquid
 310 volume).



311

312

Fig. 7: The normalized current of the tip as a function of water content in the RTIL

313

The current of the tip is normalized with the quasi-steady state current, measured at 3.7 V/Pt ref. As observed in Fig. 7, the tip current can be doubled with a very small amount of water added (2.5 vol.%). This method appears then very promising to quantify the humidity released from a material.

315

316

Since the amount of water detected close to the surface, and the amount of water diffused into the bulk solution are different, the calibration curve as shown in Figure 7 can be used as a proof of concept. To correlate the exact amount of water content released from the material, the exact tip-substrate distance should be known to establish the calibration curve.

320

5. Results

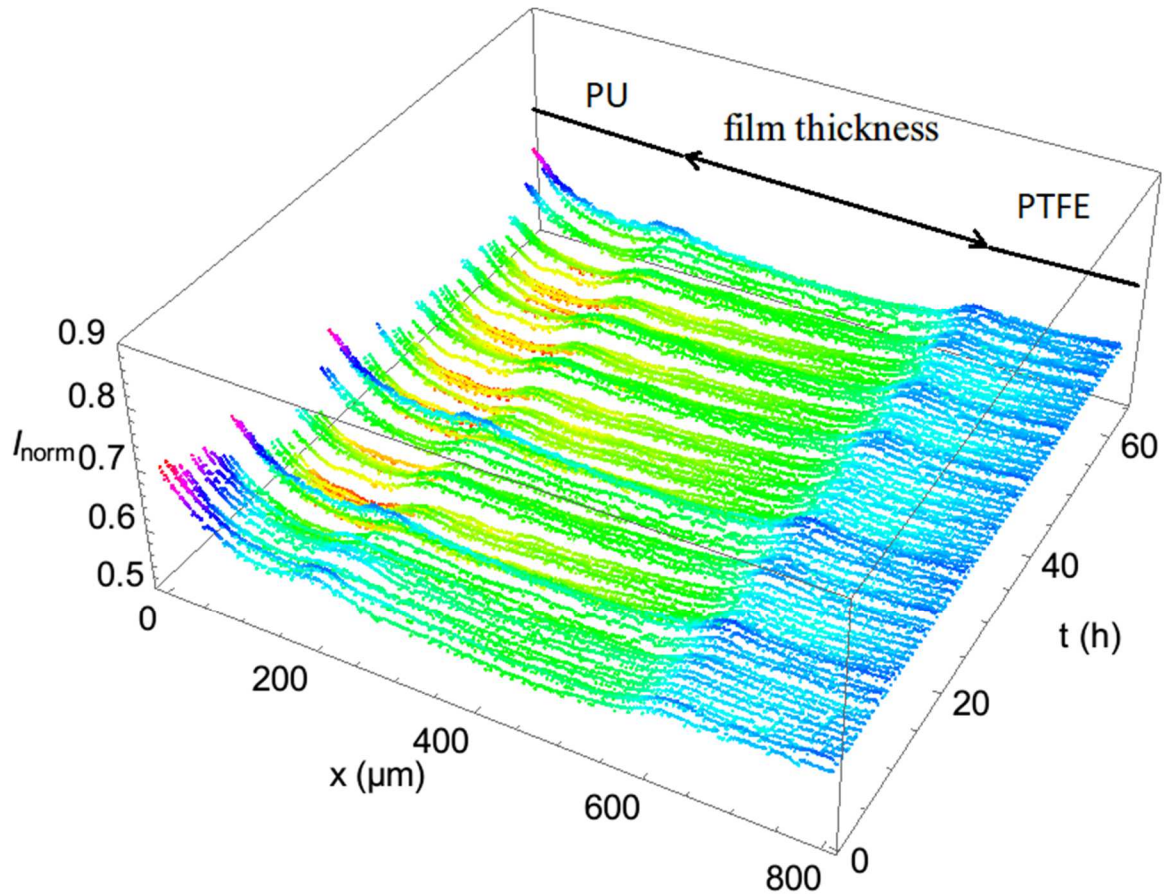
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5.1. Scan over dry resin

322

First, a dry resin specimen has been characterized in order to record a reference electrochemical behavior, in the absence of any water.

323



324

325 Fig. 8: The evolution of line scans over the dry film sample (400 μm thick) during 60 hours of RTIL
 326 immersion.

327 Figure 8 shows line scan obtained over the dry film during the 60 hours of immersion in the RTIL. The
 328 film position is shown with the arrow (thickness around 400 μm). The tip is moved from the left ($x = 0$
 329 μm) to the right ($x = 800 \mu\text{m}$). From $x = 0 \mu\text{m}$ to $x = 200 \mu\text{m}$, this is the PU part (see Fig. 2) from the
 330 sample holder and from $x = 600 \mu\text{m}$ to $x = 800 \mu\text{m}$, this is the PTFE side.

331 At the beginning, the tip current is higher due to the initial convection of the tip. Therefore, the
 332 current is normalized with the quasi-steady state current when the tip is near the end of the scan ($x =$
 333 $800 \mu\text{m}$). The center of the material is around the middle of the scan ($x = 400 \mu\text{m}$). The tip potential is
 334 kept at 3.7 V/Pt ref, the tip velocity 2 $\mu\text{m/s}$. Scans have then been repeated every 5 minutes for 60
 335 hours.

336 The line scan over a 400 μm thick dry film didn't change during the time. It can be observed that the
 337 signal is almost completely flat all over the scan distance. As the thin film is completely dry, no water
 338 is detected over the sample thickness (from $x = 200 \mu\text{m}$ to $x = 600 \mu\text{m}$). A slight slope is noticeable,
 339 attributed to the tilt of the sample surface. Such a tilt is not surprising considering the relatively big
 340 size of the characterized zone.

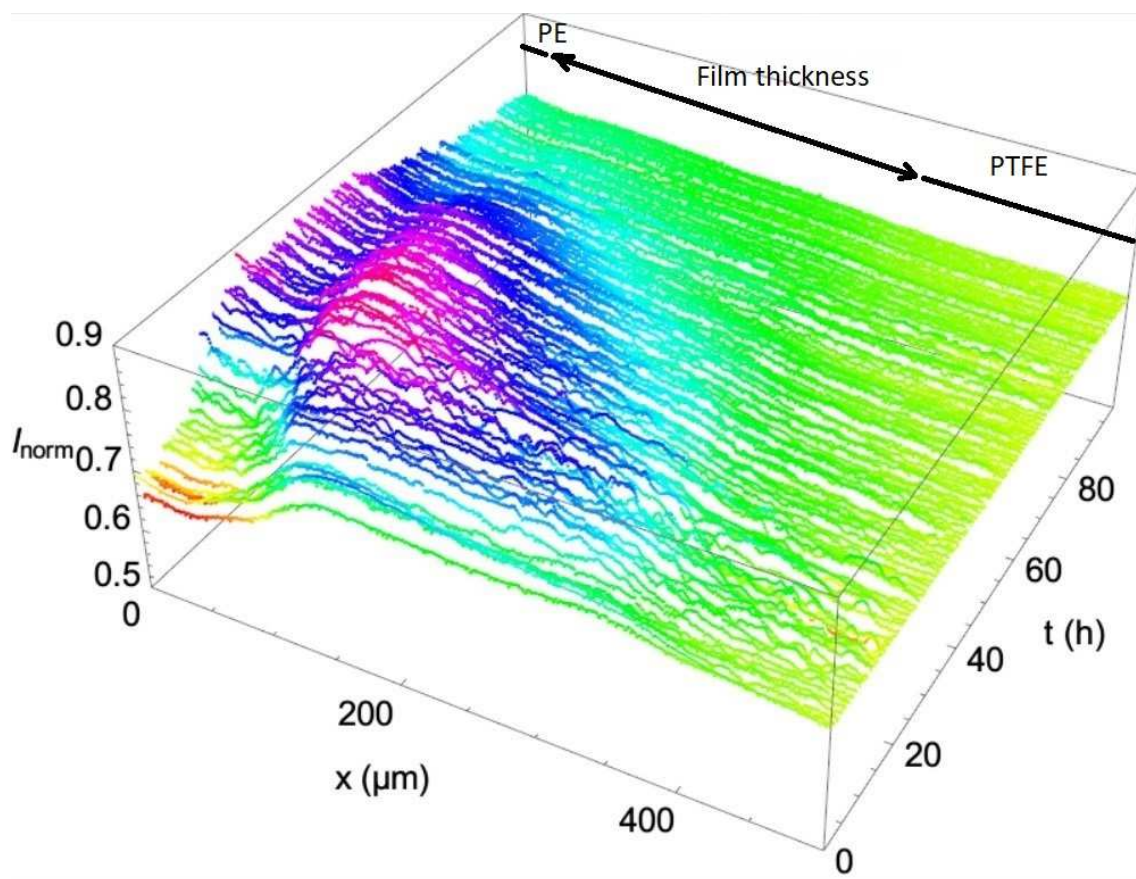
341 Only two small peaks can be observed. The distance between these two peaks corresponds to the
342 thickness of the characterized sample. They can be attributed to topographic variations, easily
343 explained by the non-ideal interface between the sample and the sample holder. The scan profile is
344 stable over the whole period of characterization. Indeed, no evolution of the current is observed up
345 to 60 hours. It is consistent with the absence of water and the characterization of a dry sample. It
346 also attests that the setup is efficient to prevent the ingress of external water from the air.

347

348 5.2. Scan over water saturated resin

349 A water saturated resin specimen has been characterized in the same conditions in order to evaluate
350 the ability of the method to detect the presence of water. Scans have been performed every 5
351 minutes for more than 90 hours. Figure 9 shows the scan signal obtained in these conditions for the
352 saturated film sample. The film position is marked with the arrow.

353



354

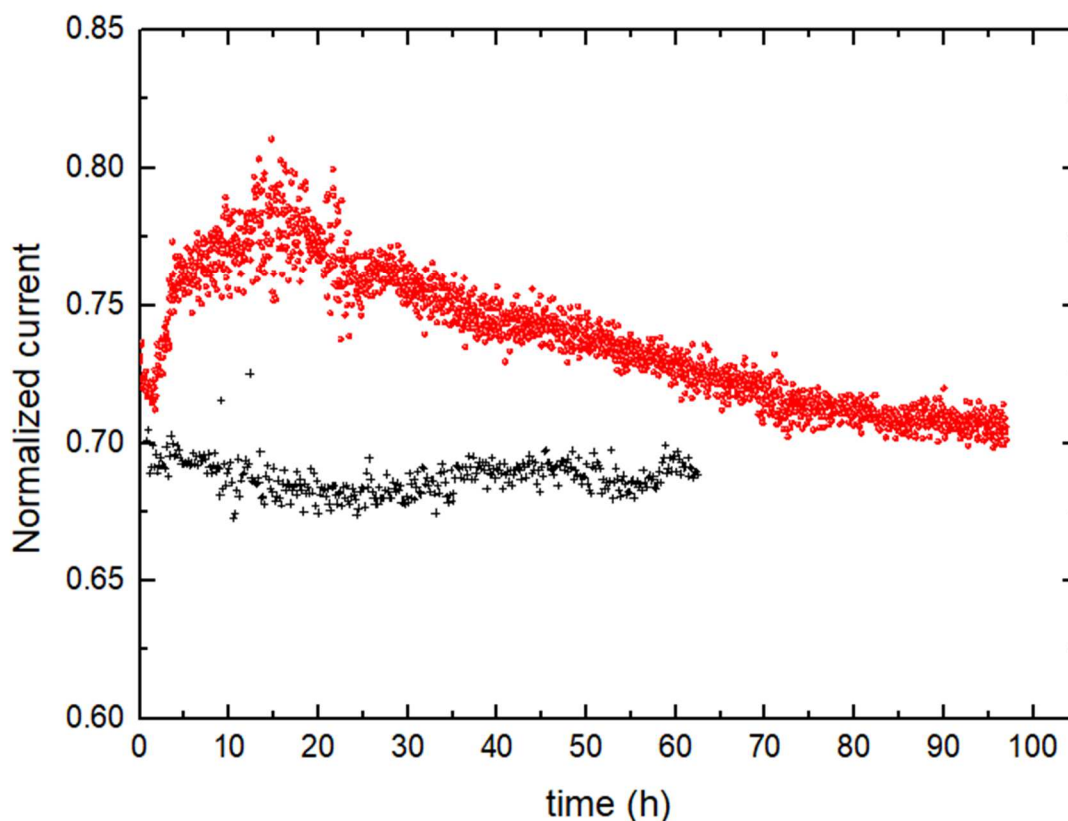
355 Fig. 9: The evolution of line scans over the saturated film sample (250 μm thick) over 4 days of RTIL
356 immersion

357 The difference with the signal previously obtained on the dry sample is significant. The signal is not
358 flat, as its value is higher over the resin material compared to the baseline. During the first 20 hours
359 of immersion, the tip current over the wet sample surface increases from $x = 150 \mu\text{m}$ to $x = 400 \mu\text{m}$,
360 which corresponds to the film thickness. This increase is due to the release of water from the wet
361 film to the RTIL environment. Indeed, the presence of water locally decreases the viscosity of the
362 RTIL, increasing the tip current (due to enhanced diffusion coefficient of the redox specie). Though a
363 symmetric profile could be expected, the topography and the tilt of the sample may have disturbed
364 the ideal shape of the profile, resulting in slightly dissymmetric curves. Indeed, a slight tilt of the
365 sample surface has to be considered, as well as for the dry sample presented above.

366 After 80 hours of immersion, the tip current above the sample has become flat. This can be
367 interpreted as there is no more water released from the sample after a very long period of
368 immersion. Compared to figure 8 for the dry film (at the same scale), a signal peak can be observed
369 above the wet film.

370 5.3. Evolution of the current signal over time

371 The evolution of the current response over immersion time in the RTIL for dry and saturated
372 specimens has been investigated. The variation with time of the normalized current measured in the
373 center of the sample has been plotted, as shown on figure 10.



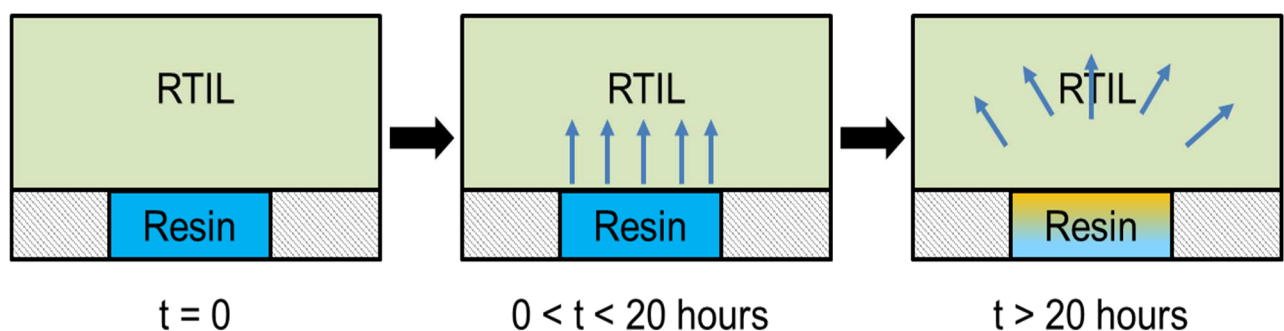
374

375 Fig. 10: Evolution of the normalized current in the center of the samples versus immersion time in
376 RTIL (red: saturated film, black: dry film)

377 The difference is clear. The dry specimen confirms its stable behavior with a constant value of the
378 normalized current all over the immersion period.

379 Comparatively, the normalized current measured for the saturated specimen significantly evolves. A
380 sharp increase from 0.7 to approximately 0.8 is observed during the first 15 hours. Then, the
381 normalized current value slowly decreases down back to a value of 0.7. Such an evolution can be
382 explained and described as schematized in figure 11.

383



384

385 Fig. 11: Illustration of the different steps involved in the evolution of the current observed on the
386 water saturated resin. Blue arrow: flux of desorbed water

387 At the beginning of the immersion in the RTIL, few water molecules had time to desorb and reach the
388 neighborhood of the microelectrode, which is $5 \mu\text{m}$ away from the surface. As time goes by, water
389 progressively desorbs and diffuses in the RTIL, increasing the tip current value. The maximum of the
390 current value corresponds to the moment at which water has fully desorbed from the resin. From
391 this point, water continues diffusing to the bulk of the RTIL, while no more water molecules are
392 provided by the sample. Indeed, the diffusion of water molecule is faster in the RTIL than in the resin,
393 inducing the progressive decrease of the normalized current value back to its initial value.

394 To evaluate the rate of water release, it is necessary to establish a calibration curve with the same
395 operational condition (tip-to-substrate distance, temperature, the range of water content). Figure 10
396 can also be used to calculate the amount of water released by comparing the base line (for dry film
397 resin) and the rate of water release as a function of time (red point for the saturated film). The
398 profile of water released over the material surface can also be compared between the simulation
399 obtained by COMSOL Multiphysics and the experimental result obtained by the SECM. These points
400 are currently under investigation in our lab.

401

402 **6. Conclusions**

403 In this work, we proposed a new experimental protocol to evaluate the humidity profile in a
404 polymeric material using SECM in RTIL medium. A sample preparation process has been proposed in
405 order to keep the water concentration of the specimens as close as possible to its state before
406 removal from immersion in water. In particular, the use of fast and room temperature processes for
407 the sample preparation allows to preserve the water distribution in the samples.

408 Dry and saturated samples have been compared according to the proposed methodology. Obtained
409 results emphasize the sensitivity of the SECM technique to the water concentration at the
410 microscopic scale. From the evolution of the current signal over immersion time in the RTIL, it can be
411 deduced that a window of approximately 20 hours is available for the characterization of the
412 humidity profile. For longer periods of time, water molecules would no longer be released by the
413 specimen and water will just diffuse to the bulk of the RTIL. The duration of this window would of
414 course be influenced by the nature of the resin and of the RTIL. When working with high viscosity
415 ionic liquid, slow scanning speed is required to reduce the velocity. This is the possible drawback of
416 this approach when a large sample is scanned. The time required to perform the 2D scan with such a
417 slow scanning speed could be too long.

418 The method provides a benefit over the conventional analysis providing the possibility to detect the
419 water content over a thin epoxy resin surface. Based on a scanning electrochemical tip, the water
420 content released from the sample surface can be estimated. The quantitative relation between the
421 water content and the tip current was successfully established. Unlike optical measuring, which can
422 only be used on transparent materials, this method can be applied to both transparent or non-
423 transparent material. A good resolution of the humidity profile over a 400 μm film thickness has
424 been also obtained.

425 **Declarations**

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430 **Conflicts of interest**

431 The Authors declare that there is no conflict of interest.

432 **Availability of data and material**

433 Not applicable

434 **Code availability**

435 Not applicable

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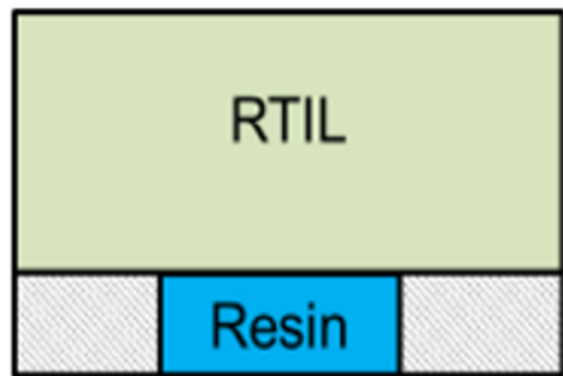
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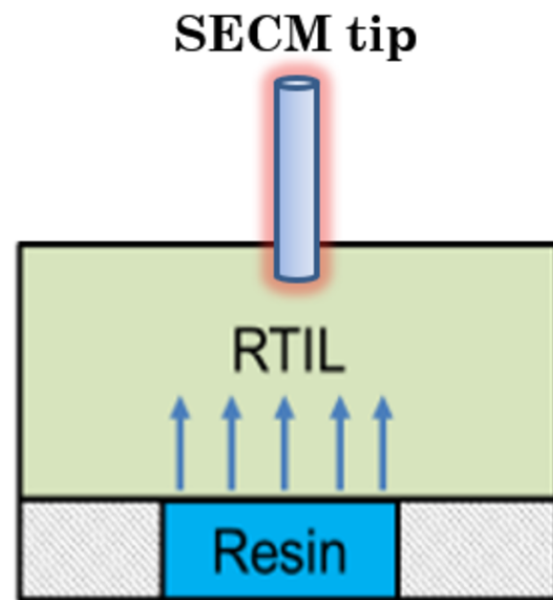
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Water saturated resin

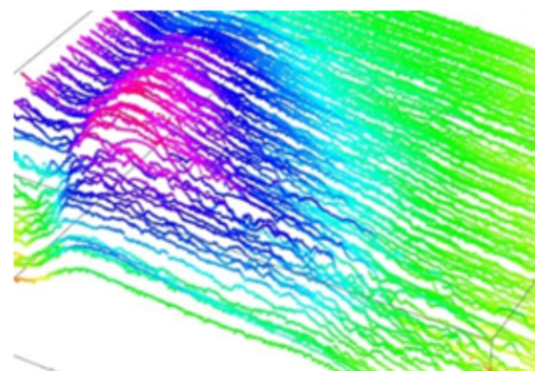


$t = 0$

Probing moisture gradient



$0 < t < 20$ hours



Observing water content coming from the resin