Effect of hygroscopic atmospheric particles deposition on the corrosion reliability of electronics

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Abstract
Atmospheric corrosion of printed circuit board assembly (PCBA) surface is synergistically affected by many factors, such as temperature (T), relative humidity (RH), chemical composition of atmospheric contaminants and electric field.
In this work, a prototype rotating impactor was developed to deposit sub-micrometer atmospheric particles contaminants on surface insulation resistance (SIR) patterns for a minimum of 24 hours. The test boards were exposed to varying RH conditions (30→99→30% RH) with different RH ramping rates and T. Water film formation was monitored by impedance response at 1kHz, whereas the corrosive behavior was investigated under 5V DC bias. Particles chemical composition of the water-soluble (WS) inorganic fraction and mono- and di-carboxylic acids were characterized by means of ion chromatography from $PM_{2.5}$ samples.
Thin electrolytic-layer formation due to deliquescence of WS compounds (about 40% in mass) abruptly decreased the impedance measured during increasing RH ramp, whereas it showed a hysteresis comparing with the response at decreasing RH ramp. The RH value at which sharp change in impedance observed was affected by T of the surrounding air and RH ramping rate. The formation of conductive layers leads to tin corrosion far below the condensing conditions. High leakage current values were observed even below 70% RH due to particles hygroscopicity and SEM-EDS analyses highlighted tin migration.

Introduction
Particle corrosion prevention is an emerging topic due to the growth of the relative importance of atmospheric particles pollutants in respect of gaseous compounds such as SO_2[1] . Ferrero and co-authors (2013)[2] highlighted the importance in take into account the synergistic role of humidity and hygroscopicity of atmospheric particles. In fact, the hygroscopic compounds can adsorb moisture and enhance the formation of a thin water layer on surfaces. In addition, water-soluble compounds which form the particles can pass from solid to liquid phases.
The synergic effects of the contamination and the air humidity on the PCBA was investigated by many authors. Sherlock and Britton (1973)[3] found that nitrates enhance tin dissolution, therefore increase the corrosion rate. Warren et al. (1989)[4] observed ECM at 76% RH on α-alumina substrates contaminated with $CuCl_2$. Frankenthal et al. (1993)[5] identified 75% RH

(at 373 K) as the threshold condition above which the formation of $Cu_4(SO_4)(OH)_6$ is observed for copper specimens contaminated with submicron-sized $(NH_4)_2SO_4$ particles. Verdingovas et al. (2014)[6] investigated the effect of NaCl contamination at different RH and temperature (T) on surface insulation resistance (SIR) comb pattern measuring leakage current (LC) biased at 5 V DC. The authors observed a strong increase in LC above 75% RH at room T. Lately, Verdingovas et al. (2015)[7] pointed out the effects of five weak organic acids – namely adipic, succinic, DL-malic, glutaric and palmitic acids commonly used in no-clean fluxes – on LC finding RH thresholds above which LC started to increasing abruptly. These studies highlighted the role of the deliquescence of the contaminants on corrosion, since it implies the formation of an electrolyte solution and the increase in the electrical conductivity of the moisture film on the PCB surface. As a consequence, decreasing in performance of the electronic components can happen due to higher LC and shorts[8].

Contrary to a situation in which a security threshold can be easily identified since just a pure compound contaminates the circuit, ambient contaminants present a more complex chemical composition[9]. Considering the liquid or solid particles suspended within the troposphere (with a diameter between few nanometers up to hundreds of micrometers, i.e. atmospheric particles), their chemical composition varies in time and space because of the different sources and chemical reactivity [9]–[11]. The key role of these contaminants is due to the hygroscopic behavior of many compounds, mostly inorganic ionic ones, forming atmospheric particles, which enhances the formation of a thin water layer on the circuit surfaces.

D'Angelo et al. (2016)[12] showed that atmospheric particles can easily deliquesce even below 70% RH. This suggested that electrolytic layers can be developed far from water condensing conditions. This paper represents a preliminary investigation of the effects of deliquescence of atmospheric fine particles (i.e. $PM_{2.5}$) on the corrosion of printed circuit boards.

Methods
SIR patterns contaminations

The effects of atmospheric particles contamination were studied on a lead-free hot air solder levelled (HASL) surface insulation (SIR) patterns. Overall surface area of the SIR pattern was 13 mm x 25 mm. The width of conductive lines and the spacing in-between the lines were 0.3 mm. The nominal square count (ratio of total length of opposing faces and the spacing of segments) of SIR pattern was 1476.

A cascade impactor (Sioutas Personal Cascade Impactor, four impact stages, particle size cut-point: 2.5µm, 1.0 µm, 0.5 µm, 0.25 µm and a filtering stage) was modified in order to deposit a round spot with a diameter of 2.0 cm, by means of a mechanism which allowed the complete rotation of the line-shaped nozzle in less then 6 min. The airflow rate was set constant at 10 L min-1 by means of a vacuum pump. The SIR patterns were removed from the PCBA and housed at the lowest impaction stage (nominal particles size range: 0.25 – 0.50 µm) to deposit the finest fraction possible, which was shown that represents an important mass fraction within the atmospheric particles size mode [13], [14]. In addition, the finest particles are recognized being the most hazardous fraction due to the fact that they can easily bypass filtering systems [2].

In order to avoid the deposition of liquid particles, the airflow was forced passing through an airflow-tube dryer before entering inside the modified ROTating impactOR (hereinafter called ROTOR).
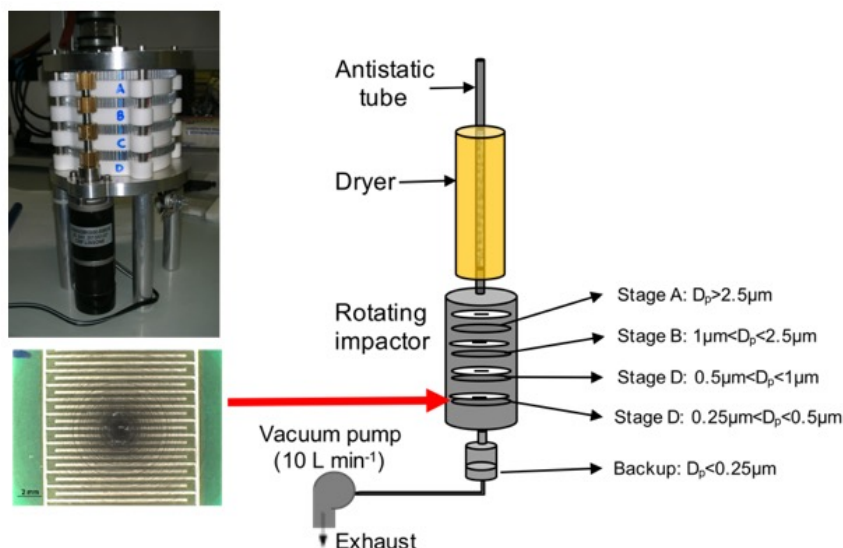
Figure 1 The rotating impactor (ROTOR) used for deposit atmospheric particles on SIR patterns.

<u>Climatic chamber and exposure conditions</u>

Contaminated SIRs patterns were exposed to increasing and decreasing RH conditions in the ESPEC PL-3KPH climatic chamber. The RH ramp was gradual and continuous in the range of 30-99% RH with a variation rate of 0.49% RH min^{-1}. The fluctuations in temperature – set at 298 K – and RH in the climatic chamber during the testing were below $\pm0.3°C/\pm2.5\%$ RH, as specified by the manufacturer. Prior to experiments, the samples were stored inside a desiccator for 48 h at low RH condition (<15% RH). At the beginning of experiments, climatic chamber was programmed to keep for 1 h at 30% RH: in the last 30 min measurement equipment recorded data in order to be sure that the contaminants where completely in equilibrium with the air conditions.

Moreover, three SIR patterns contaminated with atmospheric particles were exposed to three RH ramps with different variation rate (Sect. 4.1), i.e. 0.49% RH min^{-1} (2h 20min for each ramp), 0.10 % RH min^{-1}(12h) and 0.05 % RH min^{-1}(24h). Between each cycle, the chamber was kept at 30% RH for 1 hour allowing to the samples to reach the equilibrium with the surrounding air. Further, three SIR patterns were also exposed to three RH cycles (rate 0.49 RH min^{-1}) setting surrounding air temperature at 281 K, 298 K and 308 K (Sect. 4.2).

2.3 Impedance measurements and corrosion tests

Formation of thin water-layers on the PCB surface was followed by measuring impedance at 1 kHz frequency with a 25 mV sinus amplitude. The impedance at 1 kHz frequency is dominated by the capacitance between the SIR lines, when RH is low (below deliquescence RH of the contaminants). However, when RH increases, water layer starts to build up and contamination deliquescence, the measured impedance becomes dominated by the resistance of water layer between the lines rather than capacitance. In this case, a significant reduction in impedance corresponds to the deliquescence of the particles and increase in water layer thickness.

The measurements were performed with a "BioLogic VSP" potentiostat at 1 kHz frequency and with 25 mV sinus amplitude.

ECM is typically studied applying constant voltage and measuring LC through not-linked electrodes [15]. In this circumstance, "BioLogic VSP" potentiostat was used to record the low current passing through a conductive layer. Thus, 5 V DC was applied to SIR patterns and LC was recorded within increasing and decreasing RH ramp (30.0-90.0% RH).

2.3 Chemical analyses

Morphology of corrosion products and tin dendrites after the LC measurements was characterized by means of scanning electron microscope (SEM JEOL 5900 instrument) and analyzed for elemental composition with energy dispersive spectroscopy technique (EDS Oxford Link ISIS).

In order to chemically characterize the water-soluble (WS) fraction of collected contaminants, atmospheric $PM_{2.5}$ was collected on PTFE filters (Millipore®, Ø=47 mm, PMP ring, 2 µm porosity). The method is described in details elsewhere[16]. The analyses focused on the evaluation of: Na^+, K^+, Ca^{2+}, Mg^{2+} NH_4^+, F^-, acetate, formiate, Cl^-, succinate, NO_3^-, SO_4^{2-}, oxalate and PO_4^{3-}.

Results and discussion

The effects of humidity and hygroscopic particles on impedance measurements

An example of the impedance response due to the changes in surrounding air RH conditions for a SIR contaminated with atmospheric particles is shown in *Figure 2*. An early water uptake was commonly observed leading to an impedance decrease. Further increase in RH caused a drop in impedance within the range of 55.0-63.0% RH. Above this range, impedance continued to decrease with the RH increasing, reaching an impedance values below 20 kΩ at 90.0% RH. During the decreasing RH period, firstly, a slow increase in impedance was observed, then a faster one was recorded suggesting a re-crystallization of water-soluble compounds within the range of 50.0-44.0% RH and then a complete water evaporation.
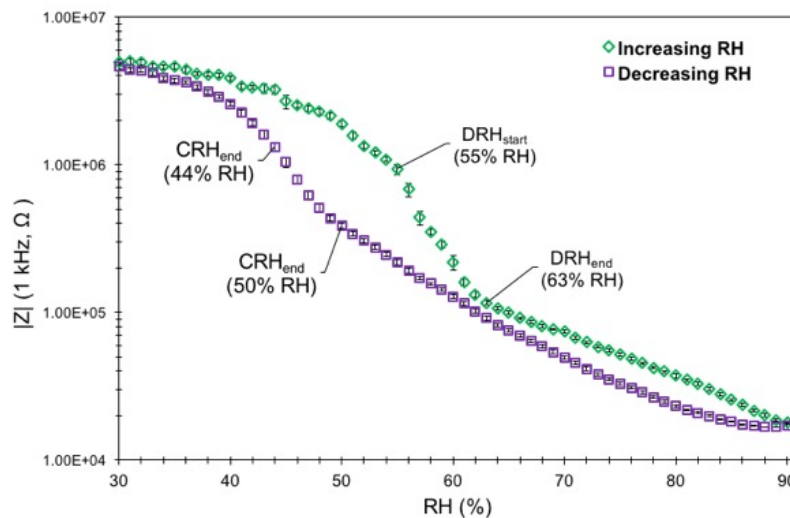

Figure 2 Impedance responses for a SIR pattern contaminated with atmospheric particles.

The analyses carried out on 9 SIR patterns contaminated with atmospheric particles indicated that the DRH occurred within 51.7±2.9% RH and 59.0±4.5% RH range at 298 K. Evaporation, which occurred while drying the air inside the climatic chamber cause reduction in the thickness of the water layer and increases the electrolytes concentration of the solution. Data showed that the evaporation increased the impedance until a sharp reduction was observed starting from 49.0±5.3% RH. This period, which ends at 41.5±4.8% RH, was identified as the RH range in which crystallization of the solid material occurs.

The results from ion chromatography stated that the $PM_{2.5}$ samples had a high content in nitrate (25.7±4.6% w/w) and a lower content in sulfate ions (12.1±0.6% w/w), with an average ratio NO_3^-/SO_4^{2-} of 2.1±0.5. Inorganic ionic fraction accounted for 50.1±4.8% w/w of the total mass of particles collected on filters. In addition to nitrates and sulfates, ammonium ions (10.5±1.0% w/w) represented the main specie found. Other cations (Na^+, K^+ and Mg^{2+}) and inorganic anions (F^-, Cl^-, PO_4^{2-}) accounted for less then 1% each. The organic

acids were found representing about 1.1±0.4% of the mass. These findings allow to explain the agreement of DRH and CRH identified in this work with those provided in D'Angelo et al. (2016)[12]. In fact, the authors highlighted that $PM_{2.5}$ samples with high NO_3^- contents showed DRH range between 51.6±0.7% and 58.5±0.7% RH while CRH was observed in average within 48.1±0.5 – 44.3±0.6 % RH range.

The formation and the conductive properties of the thin electrolytic layer resulted to be also affected by the RH variation rate and the temperature of the air surrounding conditions in addition to the highlights that not only the changes in RH affect the film properties.
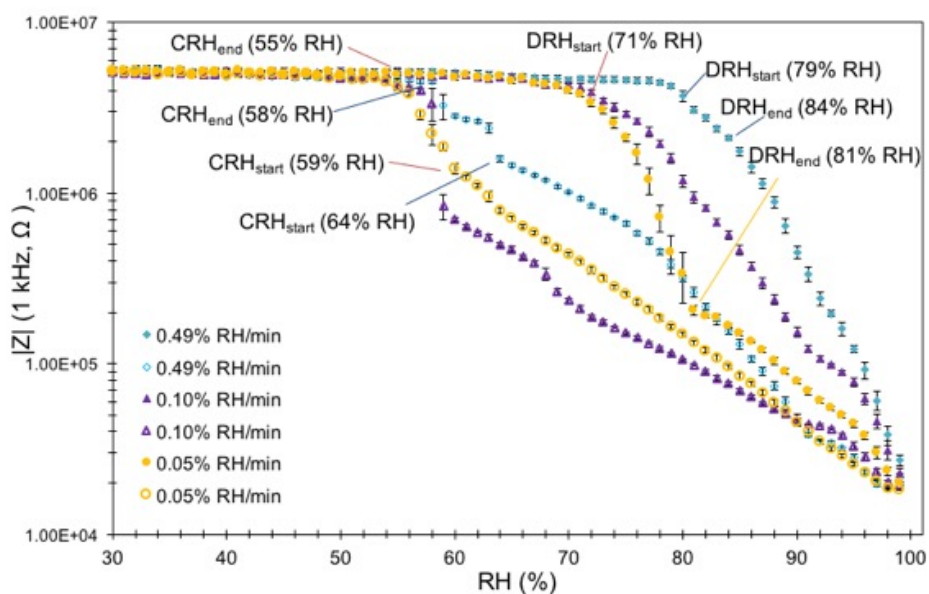

Figure 3 Impedance response for a SIR pattern contaminated with atmospheric particles exposed to three RH ramps with different variation rates.

The *Figure 3* shows the impedance profile of a SIR pattern contaminated with atmospheric particles during RH cycles at different variation rates. The curves highlighted how the DRH and CRH tend to decrease with decreasing rate of RH ramping. The results showed that there was no difference in minimum impedance reached due to the effect of water uptake. Nevertheless, after deliquescence the lower the RH variation rate the lower the impedance value reached at fixed RH.
Concerning the effects of temperature, the results clearly highlighted that both DRH and CRH decrease with the increasing in air temperature. The data analyses carried out on three SIR patterns contaminated with ambient particles suggested that there was a decrease in DRH of 0.4±0.1% RH K^{-1} and in CRH of 0.5±0.2% RH K^{-1}.
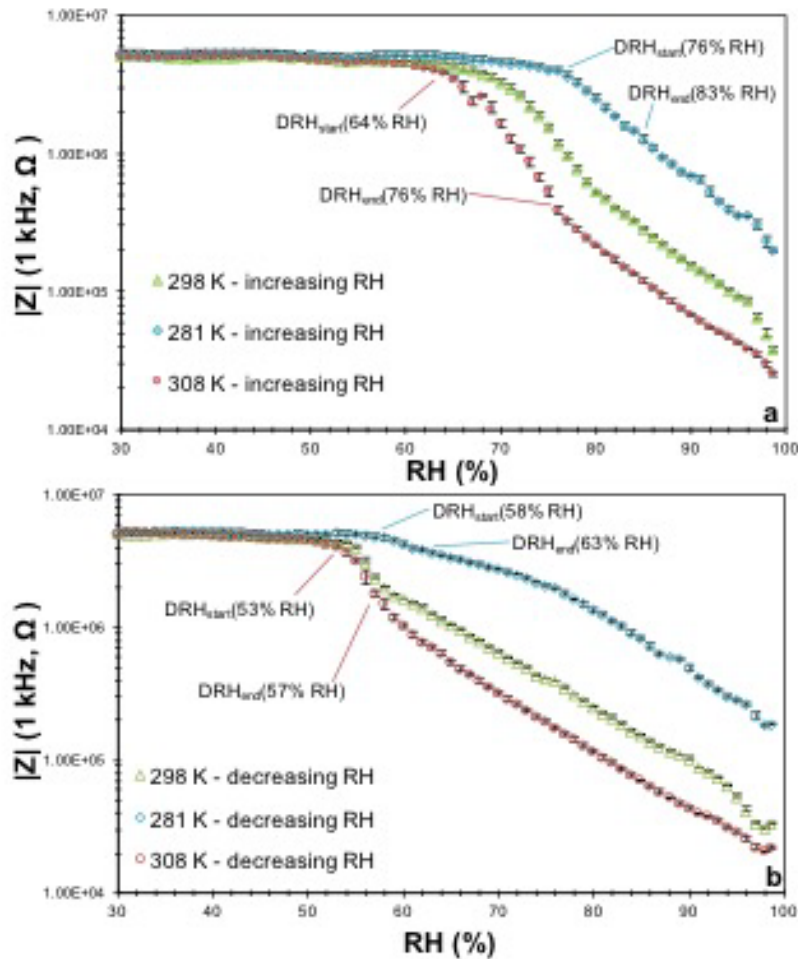
Figure 4 Impedance responses during increasing (a) and decreasing (b) RH ramp obtained at different temperatures.

Evidences of corrosion below the condensing conditions

Leakage current was measured applying 5 V DC voltage during a RH cycle from 30.0% to 90.0% RH and reverse with a single ramp duration of 2 h 20 min (rate 0.49 RH min^{-1}) at 298 K. In *Figure 5* the impedance response (Fig. 5a) and the leakage current measurements (Fig. 5b) of the same sample are shown. The impedance response revealed that atmospheric contaminants enhanced water adsorption even at low RH conditions that caused an increase in LC as well. Even though the starting RH of the deliquescence process was not clear, the impedance profile states that the end of this processes occurred at 64.0% RH. Below this threshold, the increase in LC was already observed but, starting from 64.0% RH, the LC showed a further increasing trend. This suggested that water-soluble compounds dissolved and the electrolytic layer formed on the SIR surface allowed the conduction of charges and the electrolytic cell was active (corrosion of SIR pattern).

This suggested that ECM processes can occur even far from condensing conditions. A confirm of this was provided by SEM-EDS investigations. Although no dendrite-like structures were observed, EDS revealed the presence of oxides/hydroxides and tin deposits, thus the distance between the conductive lines was shortened causing increase in LC.
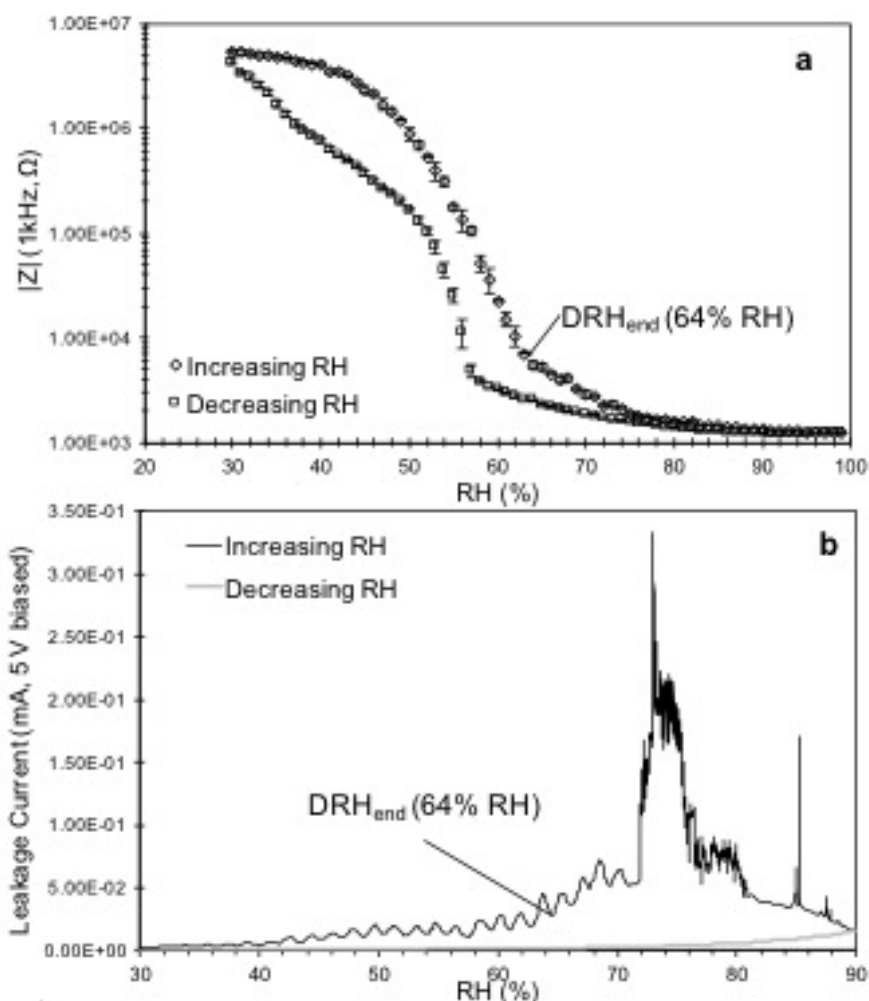
Figure 5 Impedance (a) and LC measurements (b) of the same SIR pattern contaminated with atmospheric particles.

In Fig. 5b a temporary bridge it seemed to be formed at 73% RH because of the steep increase in LC. On the other hand, at higher RH, LC decreased likely due to dendrites breakdown. Although high RH conditions were expected to promote further high LC values, with the beginning of the decreasing RH ramp, the electrical signal decreased with a similar behavior of the clean SIR pattern (Fig. 5c). Such a similar effect could be ascribed to tin passivation. On the other hand, since atmospheric contaminants are characterized by a very complex chemical composition, a clear understanding of corrosion inhibitors formed was not carried out.

In this regards, EDS analyses (*Table 1*) highlighted the presence of sulfur and oxygen forming the corrosion products. Moreover, ion chromatography carried out by the water-soluble compounds extracted from the PTFE filter – sampled simultaneously with the SIR pattern – showed many other chemical species both organic and inorganic compounds which can affected the corrosion process. In fact, Inorganic ionic fraction represents the 50.1% (mass percentage) of the collected particles mass and 1.1% is represented by mono- and di-carboxylic acids. The unresolved fraction (48.8%) was mainly represented by elemental carbon, other not-analyzed water-soluble organic and hydrophobic organic compounds. In this regards, further studies have to be carry out in order to investigate the tin passivation processes and the role of the contaminants in the promotion of it.
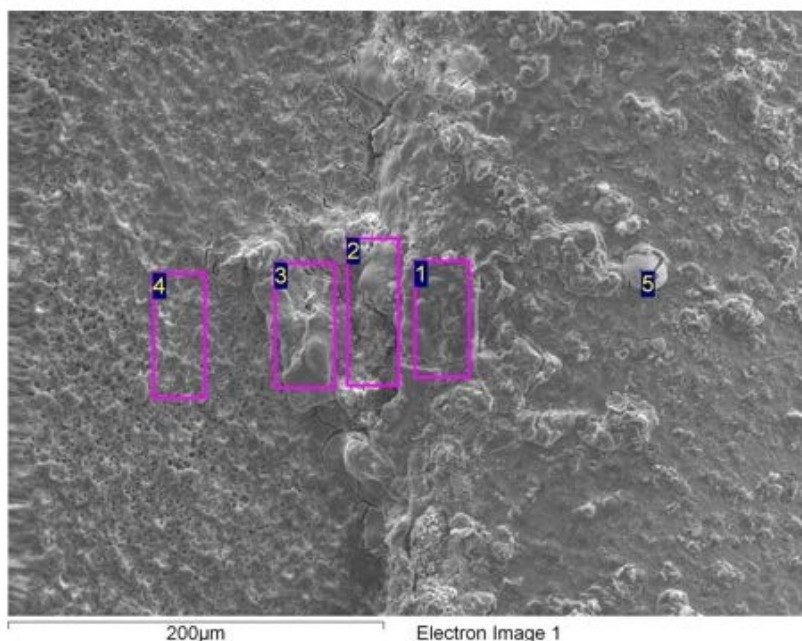
Figure 6 SEM image of the corrosion promoted by atmospheric particles and 5 V DC biased.

Figure 7 EDS results of corrosion products referring to Figure 6. All data are given in mass percentage.

Spectrum	O	Br	Si	S	Cu	Sn
1	49	<0.1	-	4	1	46
2	42	<0.1	-	5	4.6	47
3	40	-	-	5	1	54
4	44	3	0.6	4	-	48
5	33	-	-	2	-	64

Conclusions

This work provides a substantial contribution to the link between atmospheric particles and corrosion science. By means of a new prototypic device the deposition of atmospheric contaminants can be accelerated in order to carry out corrosion tests.

The results highlighted that atmospheric particles can trigger corrosion processes below the condensing conditions because the hygroscopic properties of them enhance the formation of a thin water layer on circuits surface. In this regards, the impedance measurements are able to provide information about the condition of the surrounding air that can promote solid to liquid phase transitions of water soluble compounds which form the particulate contaminants. These processes were observed to accelerate the corrosion processes because they enehance the increase of the thickness of the electrolytic layer.

Acknowledgments

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