Innovative Plasmacoatings for High Volume Conformal Coating of Electronics

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Abstract
Plasma is considered to be the 4th state of matter. Decomposed molecules interact with all exposed surfaces of the material, even the inner surfaces of open cell structures. In low pressure plasma technology, a stable and effective plasma is created by an electromagnetic discharge of a gas at low pressure and at low temperature.

Splash-proof case study:
Complex 3D-substrates were coated with a ROHS- and WEEE-compliant super hydro- and oleophobic low pressure plasma conformal nanocoating. These electronic devices were then subjected to splash-proof testing according to IEC60529. IP ratings from IPX2 to IPX4 were obtained, depending on the device's design. Acoustic performance was tested on microphones and speakers by measuring the sensitivity for a frequency range from 20 Hz to 20 kHz, and showed that the coating doesnot impact the acoustic performance. The coatings are z-axis conductive and thus obviate the use of masking and allow for flexible integration in the manufacturing process.

Waterproof and sweatproof case study:
Electronic components were coated with a 1-3 μm low pressure plasma barrier coating and were then assembled into the electronic device. A thin conformal nanocoating can be applied on the assembled product to reduce the ingress of water. These coated devices were then subjected to waterproof testing according to IEC60529. IP ratings from IPX5 to IPX8 were obtained, depending on the device's design. Short circuit testing was performed on SIR-like PCBs, measuring the current of the circuit when the powered PCB is submersed in water, salt water or artificial sweat. The short circuit current values stayed below 0.1mA, indicating no corrosion on the PCBs (4.7 V, 15 minutes submersion time).

One of the key drivers of low pressure plasma is the reduced environmental impact compared to traditional wet chemical processes and to the use of more harmful metals. The dry and clean technology has a zero-water consumption, a minimal chemical consumption and a reduced energy consumption, because no heating, drying or curing is needed. This leads to innovative low-pressure plasma coatings that can be used in many applications. The system design and size is adaptable to the dimensions of the products to be coated. In most cases there exists a suited low-pressure plasma treatment with well-dimensioned equipment to help improve protection of electronics.

Introduction
Low pressure plasma technology has been industrially applied since the early eighties. Initially it was mainly used to clean or desmear printed circuit boards, using an etching type of plasma. Gradually the technology spread into rigid plastics' industries, where polymers were cleaned and activated using pure gases such as oxygen and nitrogen. This removes organic contamination on the microscopic level by breaking the longer chains of the dirt into shorter chains that are volatile and are pumped away in the plasma exhaust. The activation creates functional groups onto the outer polymer chains of the material. These typically polar groups increase the surface energy of the plastic, while the bulk properties of the material remain unchanged. This improves the adhesion with paints, adhesives or printing inks, even on complex three-dimensional parts. Different industrial markets adopted the low-pressure plasma technology because of the higher quality performance, and the ecological and economic advantages. Plasma cleaning and activation is nowadays widely used to replace primers, or other surface treatment technologies such as flaming or corona.

The breakthrough of low pressure plasma technology in consumer electronic devices – such as headsets, wireless speakers, smartphones, smartwatches, e-readers, etc. – came with the development of plasma coating processes. These processes use plasma to polymerize monomers on the surface of the material. Plasmacoatings are deposited on the surface of components, subassemblies and assemblies, adding new and permanent functionalities to the product. Innovative plasma processes allow to deposit conformal coatings with high levels of hydrophobicity and/or oleophobicity on consumer electronics for use in humid and corrosive environments.

Together with development and improvement of low pressure plasma processes, the equipment is continuously improved as well, for better uniformity and more stable processing. The size of the system is fully adaptable to the needs of the customer, and fit into a mass production environment.

Low Pressure Plasma Technology

Plasma is considered the 4th state of matter. By adding energy matter can be transformed from solid to liquid, from liquid to gas and from gas to plasma.

In low pressure plasma technology, a stable and effective plasma is created by an electromagnetic discharge of a process gas at low pressure (and at low temperature). Under those circumstances, the process gas will be partially decomposed into radicals, electrons, photons and atoms, and is also partially ionized. All these reactive species interact with all exposed surfaces of the material. This interaction is both chemical and physical in nature. When a complex material has inner surfaces that are accessible from the outside, the plasma will also penetrate that structure to interact with these inner surfaces as well, allowing to deposit a coating throughout the structure of this 3D product.

Depending on the chemistry used, different types of processes are performed and different types of functionalities are obtained. Gases, such as oxygen and argon, are used for cleaning, activation and etching. Monomers are used to deposit coatings with certain functionalities: hydrophilic, hydrophobic, oleophobic, barrier coating, etc.The process gas is obtained from gaseous precursors or from evaporating liquid or solid monomers. A monomer supply unit ensures that controlled amounts of process gas are entered into the chamber.

The vacuum chamber is connected to a pumping group that will evacuate the chamber and maintains the vacuum during processing. In order to affect the plasma treatment in sufficiently pure process gas conditions, a base pressure in the 0.67 Pa to 6.67 Pa range is required prior to processing. Once the base pressure is reached, the process gas is introduced into the vacuum chamber and a plasma is generated. The plasma process is typically performed in a working pressure range of 3.33 Pa to 33.33 Pa.

A set of electrodes is mounted in the chamber. These electrodes are powered by a generator at a frequency of typically 40kHz, 13.56MHz or 2.45GHz and allow to create the plasma by electromagnetic discharge. The substrates to be treated are exposed to the secondary plasma outside the electrodes, where the plasma is less aggressive. The plasma power can be applied in a continuous or a pulsed mode.

Low Pressure Plasma Coating

Background

In the late nineties, low pressure plasma technology was improved to achieve polymerization of monomers on materials, depositing real nanocoatings on the surface, and adding new and permanent functionalities to the material. Innovative plasma processes allow to deposit coatings with high levels of hydrophobicity and oleophobicity on rigid and flexible materials, which can be planar (2D) or complex shaped (3D). Other plasma processes have been developed to obtain the opposite effect, by making substrates hydrophilic.

Producers of gas filter media were one of the first to adopt low pressure plasma coatings on an industrial scale. They were looking for a permanent hydrophobic and/or oleophobic effect, which can be achieved by polymerizing fluorocarbon precursors. Other markets have followed the filtration market in adopting the low pressure plasma coating technology on industrial scale. The permanent hydrophobic and/or oleophobic effects of the coatings are of great use on electronic components and devices for protection against humidity, accidental exposure to water, and corrosive environments.

The first generation of hydrophobic and oleophobic nanocoatings provide typical oil repellency levels of 3 to 4 (AATCC 118-1997 and ISO 14419).

Producers of textile products face increasing governmental pressure to replace existing wet chemical coating processes with more environment friendly technologies. The company developed together with its partners of the 6th European Framework Program ACTECO a new generation of hydro- and/or oleophobic nanocoatings allowing to obtain oil repellency levels up to 8. In order to meet the recent pressure on PFOA and PFOS, by-products in long chain perfluoroalkyl chain monomers, typically having 8 carbon atoms in the chain (C8), the company developed with its partners in a project a PFOA- and PFOS-free plasmacoating using short chain perfluoroalkyl chain monomers, typically having 6 carbon atoms in its chain (C6). With this chemistry, oil repellency levels up to 6 are achieved.

The latest trend in the durable water repellent (DWR) textile market is to move away from the use of halogen-containing chemistry.The company developed in another project with its partner a PFC-free DWR coating for textiles.

Benefit for Electronic Devices

Although originally developed for filtration textiles and other industrial textiles, the electronics market was one of the first markets to adopt the water- and/or oil repellent plasmacoatings. Damage of electronic devices, such as consumer electronics, after accidental exposure to water is the prime reason of product failure. Even short contact with water can lead to irreversible damage to electronic components, due to short circuiting and corrosion. Consumer electronics, such as headsets, are exposed to more harsh liquids than water as well, including salts and sweat.

As a result, the market is continuously looking for improved protection. A few years ago limited protection in terms of splashproofing – reduced water ingress – was sufficient, but nowadays the manufacturers and brands all request waterproof and sweatproof protection. Hydro- and oleophobic low pressure plasmacoatings allow to protect the devices on different levels. The coatings are RoHS and WEEE-compliant, donot contain SVHCs (REACH) and are bio-compatible (cytotoxicity test according to ISO 10993-5).

Splash-proof case study

Splash-proofing is the lowest protection level for consumer electronics such as wearable electronics, e.g. headsets. It requires a certain reduction of water ingress, and correlates with IPX ratings of IPX2 to 4. Water ingress protection is tested according to IEC 60529 (Table 1).

Table 1: Overview of the Water Ingress Protection (IPX) levels

IPX rating	
IPX0	No special protection
IPX1	Protected against falling water Equivalent to 3-5mm rainfall per minute for a duration of 10 minutes. Unit is placed in its normal operating position.
IPX2	Protected against falling water when tilted up to 15 degrees Same as IPX1 but unit is tested in 4 fixed positions - tilted 15 degrees in each direction from normal operating position.
IPX3	Protected against spraying water Water spraying up to 60 degrees from vertical at 10 liters/min at a pressure of 80-100kN/m2 for 5 min.
IPX4	Protected against splashing water Same as IPX3 but water is sprayed at all angles.
IPX5	Protected against water jets Water projected at all angles through a 6.3mm nozzle at a flow rate of 12.5 liters/min at a pressure of 30kN/m² for 3 minutes from a distance of 3 meters.
IPX6	Protected against heavy seas Water projected at all angles through a 12.5mm nozzle at a flow rate of 100 liters/min at a pressure of 100kN/m2 for 3 minutes from a distance of 3 meters.
IPX7	Protected against water immersion Immersion for 30 minutes at a depth of 1 meter.
IPX8	Protected against water submersion The equipment is suitable for continual submersion in water under conditions which are identified by the manufacturer.

The typical thickness of the low-pressure plasma nanocoating for splash-proofing is 50-500 nm, which enables to coat complex 3D-structures in an uniform way without any impact on acoustic performance. The coatings are z-axis conductive and thus obviate the use of masking and allow for flexible integration in the manufacturing process. They can be applied on component level, but also on sub-assemblies, assemblies and the final products.

Acoustic testing has been performed on uncoated and coated speakers and microphones. **Figure 1** and **Figure 2** respectively show the sensitivity of a speaker device and a microphone before and after coating, for a frequency range of 20 Hz to 20 kHz. It is clear from the graphs that there is no significant influence in the speaker and microphone sensitivity due to the low-pressure plasma coating applied, because the sensitivity profile is identical for speakers and microphones with and without plasmacoating.

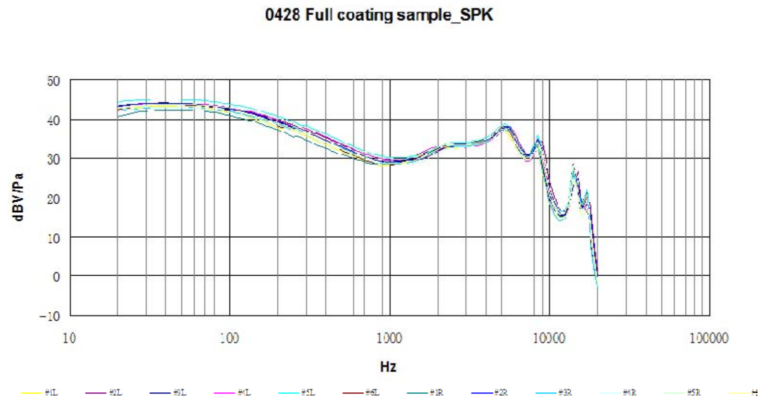

Figure 1: Sensitivity of speaker in 20 Hz – 20 KHz range

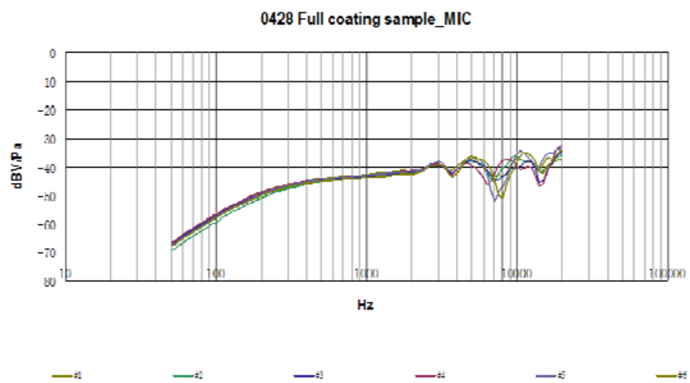

Figure 2: Sensitivity of microphone in 20 Hz – 20 KHz range

Waterproofand sweatproof case study

Consumer electronics brands and manufacturers are nowadays looking for better protection of their products against damage coming from water and sweat, i.e. they want water- and sweatproof solutions. The company developed together with a partner in a project waterproof and sweatproof coatings , which reduce considerably corrosion and short-circuiting of devices that are submersed while being powered on.

The typical thickness of these low-pressure plasma coatings is 1-5 µm, depending on the design of the product's components, the voltage and the degree of protection required. The coating is a multilayer barrier coating. IP ratings from IPX5 to IPX8 (IEC60529) were obtained, depending on the device's design (Table 1).

Due to the thickness, masking may be required on some connectors, and is required on microphones and speakers to avoid impact on acoustic behavior. The optimal degree of protection is obtained when the coating is applied on the component level, after which assembly into the final product takes place. Optionally, the assembled product is overcoated with a thin splash proofing coating to further reduce ingress of water, while the waterproof coating protects the electronic components on the inside against exposure to water while being powered on.

Short circuit test

A so-called *Short circuit test* is used to evaluate the effectiveness of the water- and sweat-proof coatings. Figure 3shows the schematic set-up: an electrical circuit is made with

- ASIR-like PCB (Figure 4); consisting of
    - An open circuit, having 2 comb patterns of 0.5mm wide copper tracks, spaced 0.5mm apart
    - An ENIG surface finish to protect the PCB against atmospheric oxidation and corrosion
- A production power supply (source meter)
- A data logger to log the current in the electrical circuit

The source meter has an auto range feature which comprises six source and measuring ranges (1A, 100mA, 10mA, 1mA, 100µA, 10µA and 1µA) with a 5% error on each source range and a 5.5% error on each measuring range. The instrument has an internal calibration which is verified by the manufacturer every 2 years. The calibration of the instrument is evaluated every month with fixed resistors to verify the reliability and functionality of the instrument.The instrument is connected to a computer (laptop) which has the necessary production software to operate the instrument and collect the data.

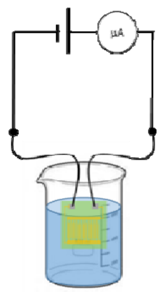

Figure 3: Schematic set-up of short circuit test

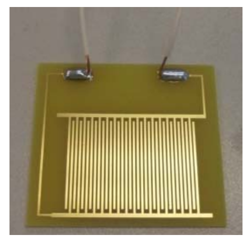

Figure 4: SIR-like PCB for short circuit test

When there is optimal protection, the resistance between both copper comb patterns is very high, and no current is detected. The PCB is submersed during the test, and the current is measured for typically 15 minutes. Submersion can be done in water, salt water and artificial sweat. The limit for visible corrosion is 0.1mA, meaning that as long as the current stays below 0.1mA, no corrosion is visible on the PCB after the test.

<u>Reference: uncoated SIR-like PCB</u>

Figure 5shows the results for the uncoated (not plasmacoated) PCB, only having an standard ENIG surface finish to protect against atmospheric oxidation and corrosion, tested according to the test conditions of Table 2. It is clear that the limit of visible corrosion is exceeded immediately, and the PCB was heavily corroded (Figure 6).

Table 2: Test conditions in water

Parameter	**Value**
Test liquid	Water (bottled water)
Applied voltage	4.7V
Test duration	15 minutes

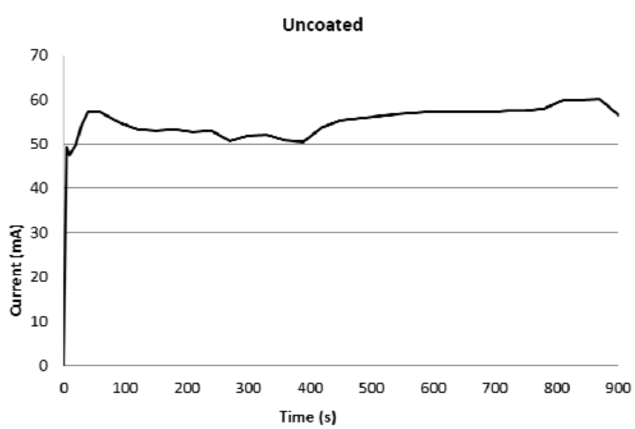

Figure 5: Short circuit current for uncoated PCB tested in water

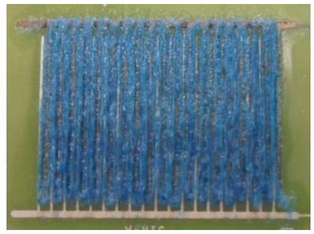

Figure 6: Uncoated PCB after short circuit test in water

Performance in water

Figure 7shows the results for a 3µm waterproof (Material A) and sweatproof (Material B) coating in water, tested with the parameters of Table 2. It is clear that the shortcut current of both coatings stays significantly lower than 0.1mA, hence no visible corrosion was noticed on the PCBs after testing (Figure 8).

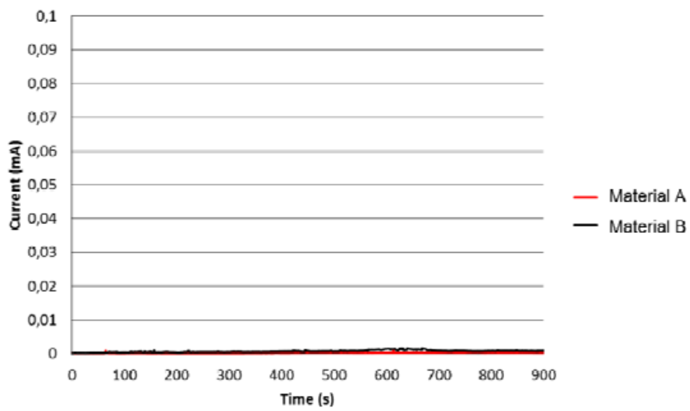

Figure 7: Shortcircuit current for 3µm coatings in water

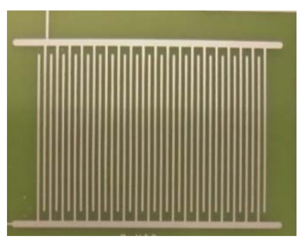

Figure 8: Waterproof coated PCB (3µm) after short circuit test in water

Performance in artificial swear

Figure 9shows the results for a 3µm waterproof (Material A) and sweatproof (Material B) coating according to the parameters in Table 3. It is clear that the waterproof coatingsexceed 0.1mA and on the PCB signs of corrosion were visible, whereas for the sweatproof coating the shortcut current stays below 0.1mA during the entire test duration.

Table 3: Test conditions in artificial sweat

Parameter	Value
Test liquid	Artificial sweat (2,5 m% Ammonium chloride; 2,5 m% Lactic acid; 1 m% acrylic acid; pH 2.1)
Applied voltage	4.7V
Test duration	15 minutes

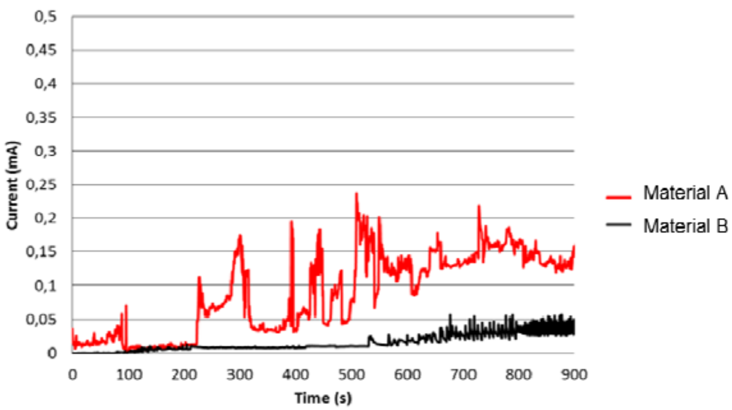

Figure 9: Short circuit current for 3µm coatings in sweat

<u>Performance in salt water</u>

Figure 10shows the results for a 3µm waterproof (Material A) and sweatproof (Material B) coating according to the parameters in Table 4. Both coatings stay below the visible corrosion limit of 0.1mA, but the sweatproof coating shows lower short circuit currents and less peaks. Peaks indicate short circuiting and other negative effects taking place.

Table 4: Test conditions in salt water

Parameter	**Value**
Test liquid	Salt water (3.57m% NaCl)
Applied voltage	4.7V
Test duration	15 minutes

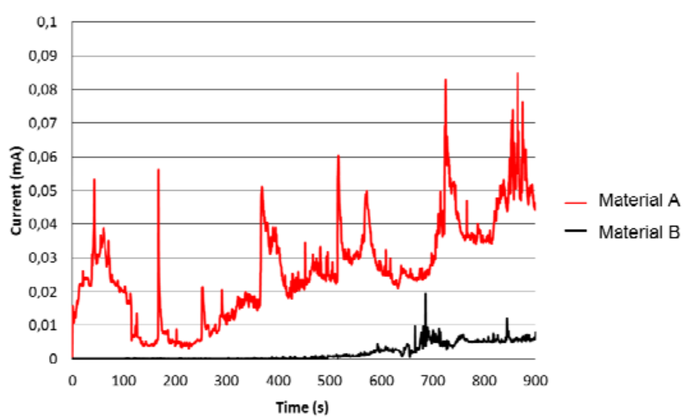

Figure 10: Short circuit current for 3µm coatings in salt water

Low Pressure Plasma Coating Equipment

Plasma systems can have all kinds of shapes and differ mostly in the loading system. Such a loading system may be a set of trays in which rigid parts such as PCBs or electronic components, subassemblies or devices are organized, or it may be a complete winding system for treating flexible materials such as flexible PCBs on rolls.

Most low-pressure plasma treatments in the electronics industry are carried out in batch processes using a tray-system for loading and unloading the machine. The design of the trays or sample holders may be optimized for the specific components, subassemblies or finished products for optimal processing and optimal loading capacity.

Figure 11shows a picture of a typical machine for low pressure plasma polymerization processes using liquid monomer precursors, suited for loading with electronic components and products. The vacuum chamber has dimensions 1000 mm x 700 mm x 700 mm, and the machine has in its standard set-up five trays of dimensions 858 mm x 672 mm x 73 mm for horizontal loading.

Figure 11: Low pressure plasma system with five trays, horizontal loading

Special loading trays to treat devices or PCBs can be designed to maximize the number of products in one batch without limiting the performance of the coating and the uniformity. Figure 12 shows a jig designed for loading 1440 PCBs – in this case control PCBs for headsets – in a single tray.

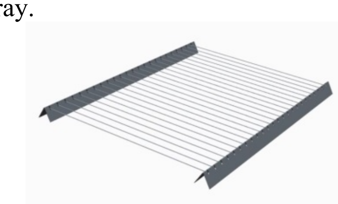

Figure 12: Loading of control PCBs for headsets

Ecological: Environmentally Friendly Processing

One of the key drivers of low pressure plasma technology is the reduced environmental impact compared to wet chemical processing.

Using pure chemicals implies a zero-water consumption, making low pressure plasma a “dry” technology, especially when compared to traditional wet processes where chemicals are mixed into (often heated) water to form solutions, emulsions and dispersions for coating application. Zero water consumption means no water effluent that needs recycling, implying substantial cost savings as well given the actual price for water and for recycling of effluents.

All processes, whether it is low pressure plasma activation, cleaning, functionalization or coating, are performed on a molecular scale, which demands relatively low amounts of chemicals. For coating processes, the consumption of chemicals can be reduced up to 80% compared to wet chemical processes such as dipping processes. Less chemical consumption reduces the number of chemical residues in the exhaust air as well. A scrubber at the exhaust is used to ensure that the concentration of components in the exhaust is below the legislatory level.

Low pressure plasma has a low energy consumption because heating is limited and far below the heating requirements in wet chemical processing that typically has a drying and curing step to evaporate the water of the emulsion or dispersion and to cure the monomers to induce polymerization. As a result, the energy consumption is up to 50% less with low pressure plasma polymerization.

Since low pressure plasma processes take place under reduced pressure, the system works in a controlled environment, where process parameters such as flow, pressure, power and temperatures are easily controlled and monitored. The operator is not exposed to the reaction chemicals because of the closed system, highly reducing the risk for accidents. Low pressure plasma is thus a “clean” technology as well.

Conclusions

Low pressure plasma technology has found already several applications in the consumer electronics industry: splashproofing, water- and sweat proofing and protecting against corrosion and short-circuiting of for example earbuds, headsets, wireless speakers and smartphones. The technology has proven to be fit for high volume manufacturing. The controlled processing environment enables a high quality, high yield production. Contrary to what many people think it is also a very cost-effective technology. Low pressure plasma technology has given the companies that use it a clear competitive edge.

It is expected that environmental legislation will drive more producers from wet chemical processing to a dry and clean technology such as plasma.

Acknowledgements

The paper makes reference to some of the results of the SME-Innovation project *PCB-Coat*, in cooperation with VUB, funded by Vlaio.

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- Application history
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- High volume manufacturing case study
- Conclusions

Application History

Large

Cleaning | Etching | Activation | Coating

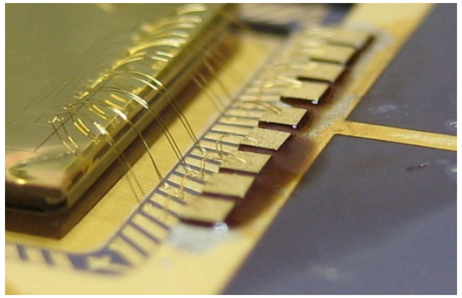
Textiles

Automotive Plastics

Medical Plastics

Electronics

System



Small

Simple — Process — Complex

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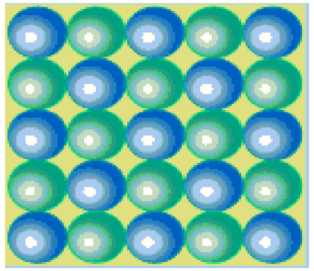
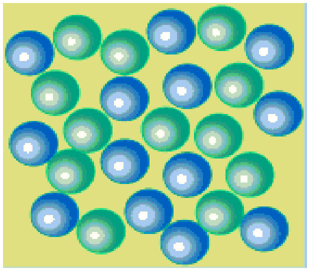
3 + 1 States of Matter

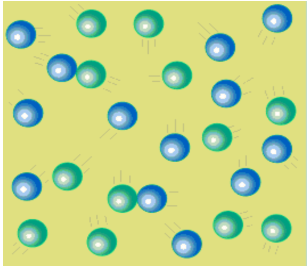
Solid



Liquid

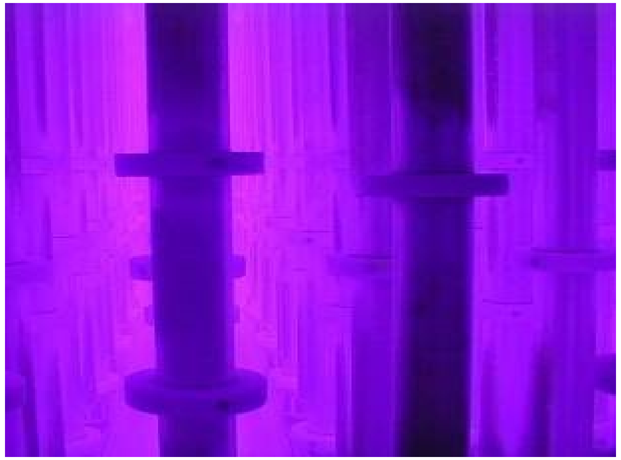


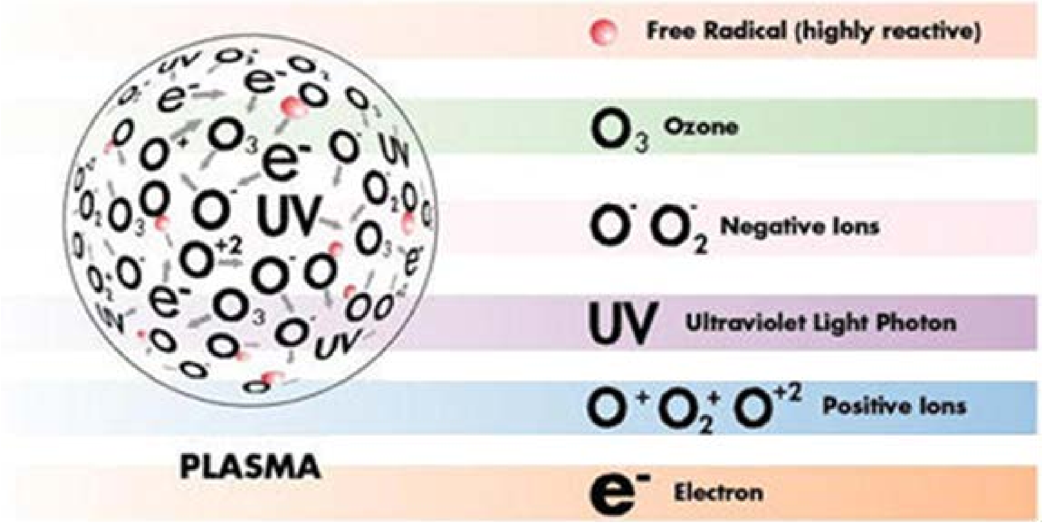
Gas



Low Pressure Plasma

- By adding energy, the molecules become more free to move until decomposed into a plasma
- Plasma is generated by an electromagnetical discharge in a gas at low pressure (and low temperature)





Plasma Polymerization

- Reaction takes place on the substrate surface
- Permanent, flexible coatings
- Typical thickness of 50 – 500 nm
- Functionality determined by precursor: hydrophilic, hydrophobic, oleophobic, barrier coatings, etc.
- Uniform coverage of complex 3D surfaces
- Penetration into core of complex shaped products

Working Principle

- Monomers with hydrophobic functional groups are used, e.g. fluorinated (meth)acrylates
- Deposition of polymer layer with nanometer thickness
- Permanent layer
- All accessible surfaces are coated throughout the substrate's structure (e.g. foams)

$$(R-(CF_2)_n-CF_3)_x$$

$$\Big\downarrow \quad \text{plasma}$$

$$CF_3-(CF_2)_n-(R-)_x$$

Consumer Electronics: Coating Type

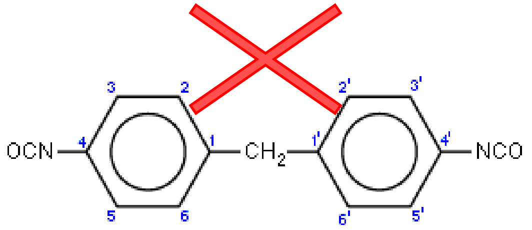
Splashproof → Waterproof → Sweatproof

Splashproof	Waterproof / Sweatproof
IPX 2 – 4	IPX 5 - 8
50 - 500nm	1 – 5 µm
Cycle Time 0,5 – 1 h	Cycle Time 2 – 3 h
Applied on Component, PCB or Device	Applied on Component or PCB
No Masking Required	Masking Depends on Application

Environmental Benefits

Every kg of plasma coating chemistry may prevent:

- 5 kg DWR (Durable Water Repellent) coating chemicals;
- 115 liters of waste water;
- Up to 1 kg crosslinking agent; i.e. Iso-cyanates
- 150 kWh energy and reduced CO2 emission
- Use of Chloride (VCM-Vinyl Chloride Monomer) in DWR
- Use of Formaldehyde



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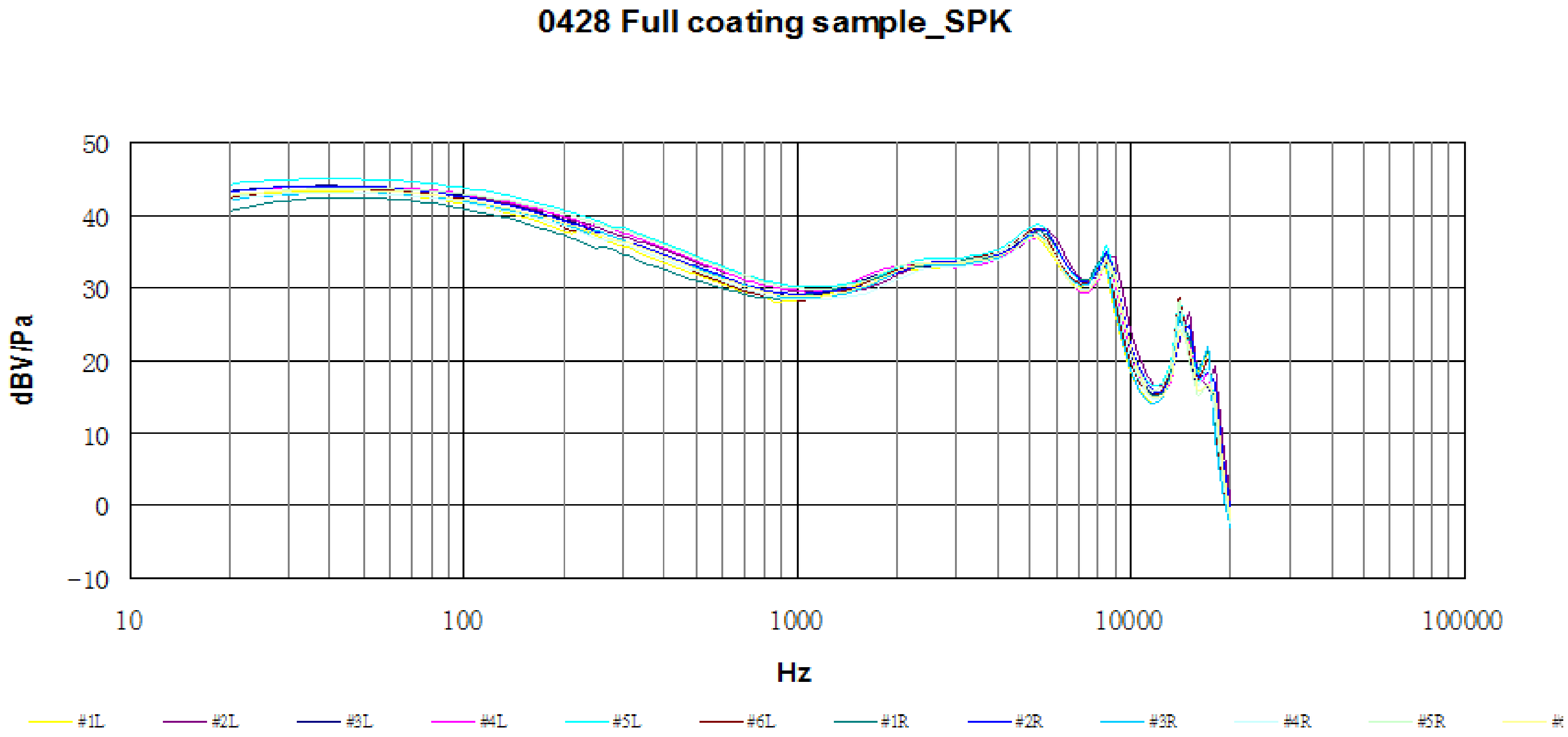
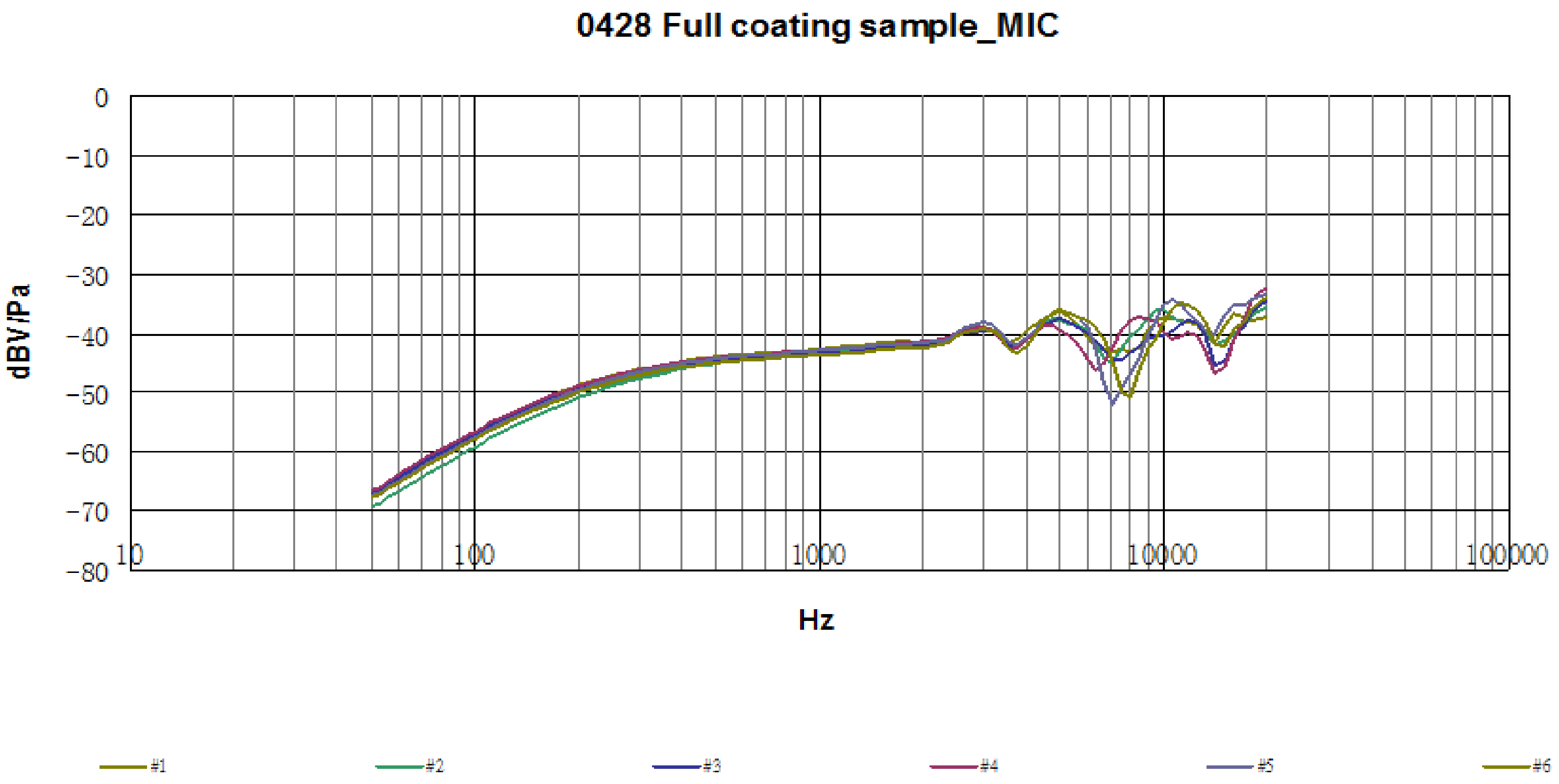
Technical Characteristics

- Single layer coating
- Thickness range: 50 – 500 nm
- Reduction of water ingress (IPX2 – IPX4)
- No influence on acoustic behaviour
- No impact on good working of micro devices
- Coatings have z-axis conductivity (flexibility in manufacturing process)
- Coatings can be soldered through
- Easy to rework

Acoustic Performance (1)

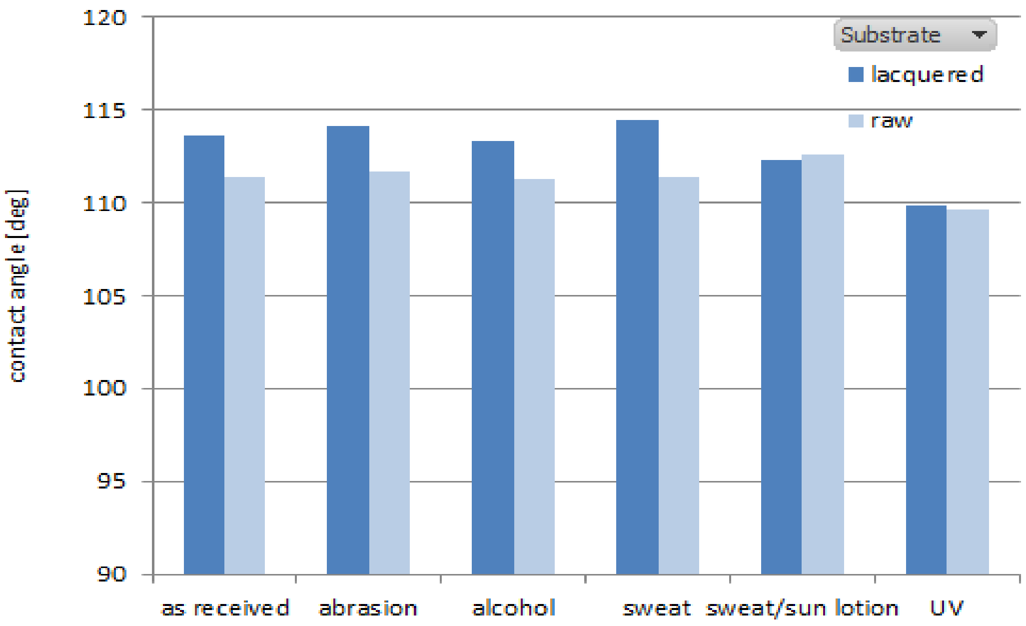


Acoustic Performance (2)



Abrasion Characteristrics

- Tested on 2 types of plasma coated PA plates (250nm coating)
- Exposure to different environments
- Uncoated sample: Water contact angle of 80,7°



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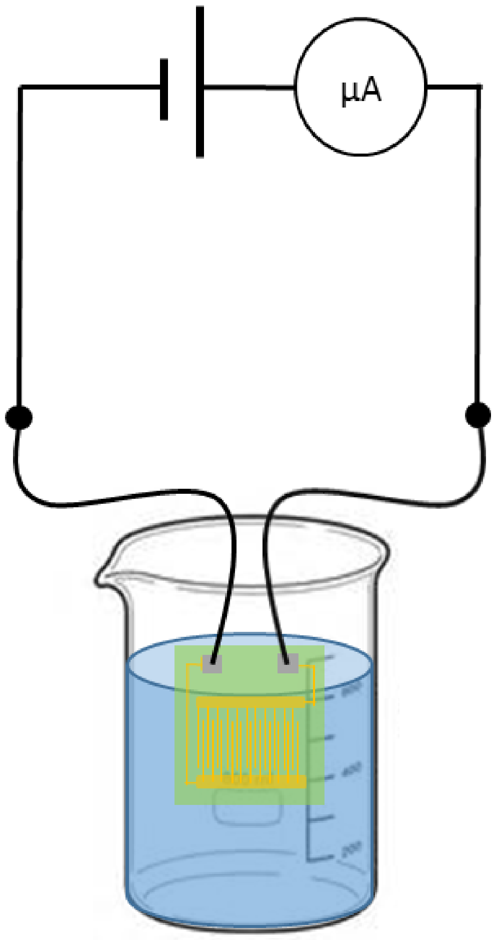
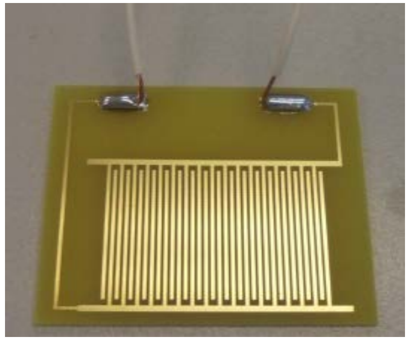
Technical Characteristics

- Multi-layer barrier coating with hydrophobic top layer
- Thickness range: 1 – 5 µm
- Protection against corrosion and short-circuiting when device is submersed while being powered on
- IPX5 – IPX8, depending on product design
- Applied on component and PCB level
- Masking depends on application and design
- Optionally thin overcoat of device after assembly

Shortcut Test

- Immersion test to test corrosion protection on a powered PCB while submersed
- Applied voltage: 4.7V
- Test duration: 15 mins
- Liquids: water, salt water, artificial sweat
- **PASS:**
  - Current <0.1mA
  - No signs of corrosion

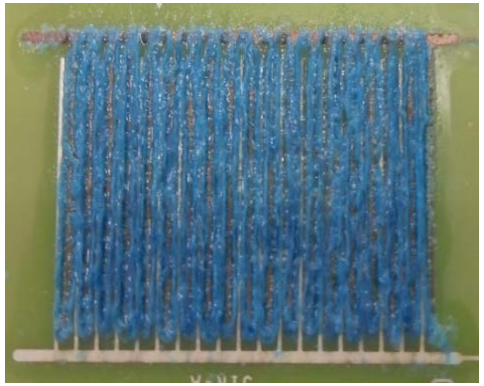


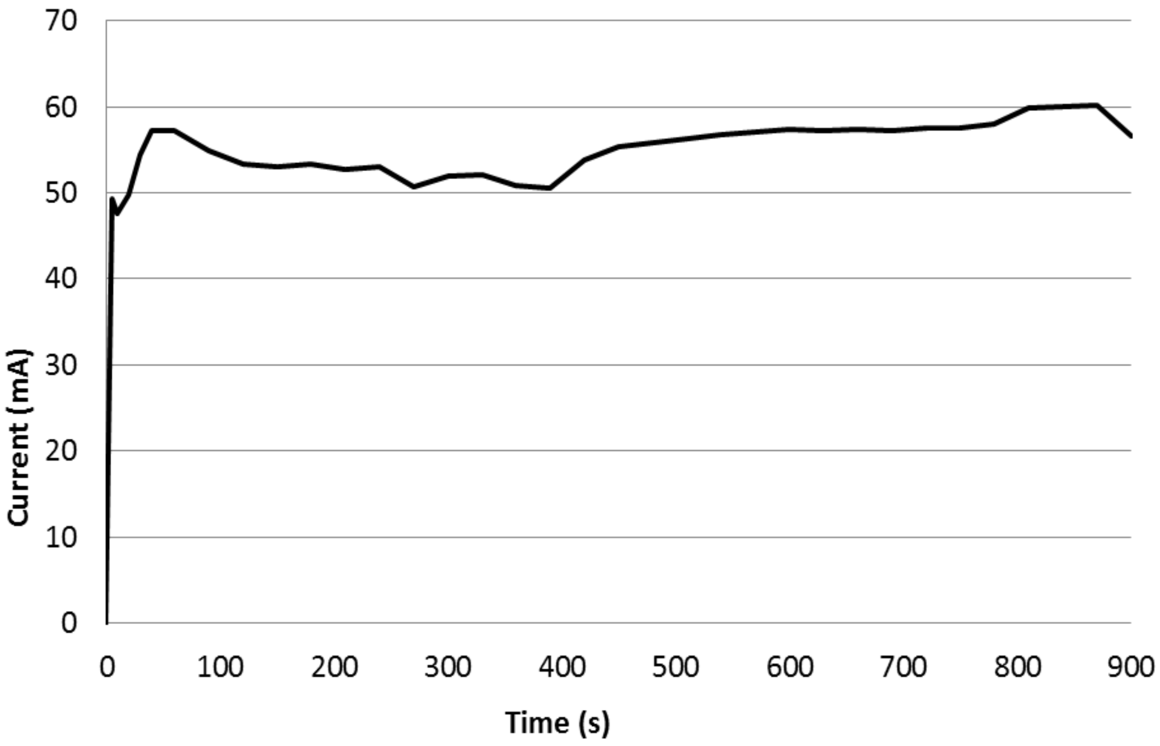


Track width: 0.5mm
Pitch: 0.5mm

Submersion in Water (1)

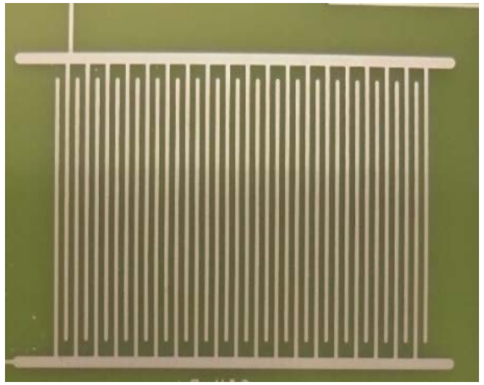
- Uncoated PCB is heavily corroded after testing
- 4,7V

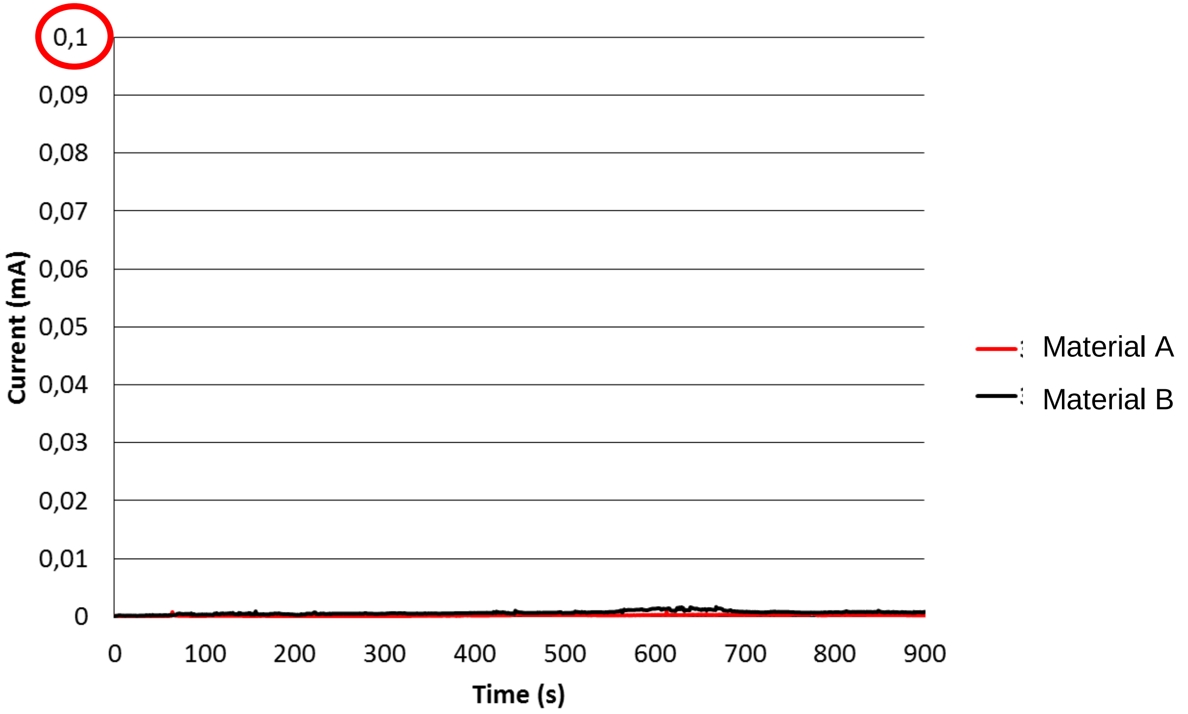




Submersion in Water (2)

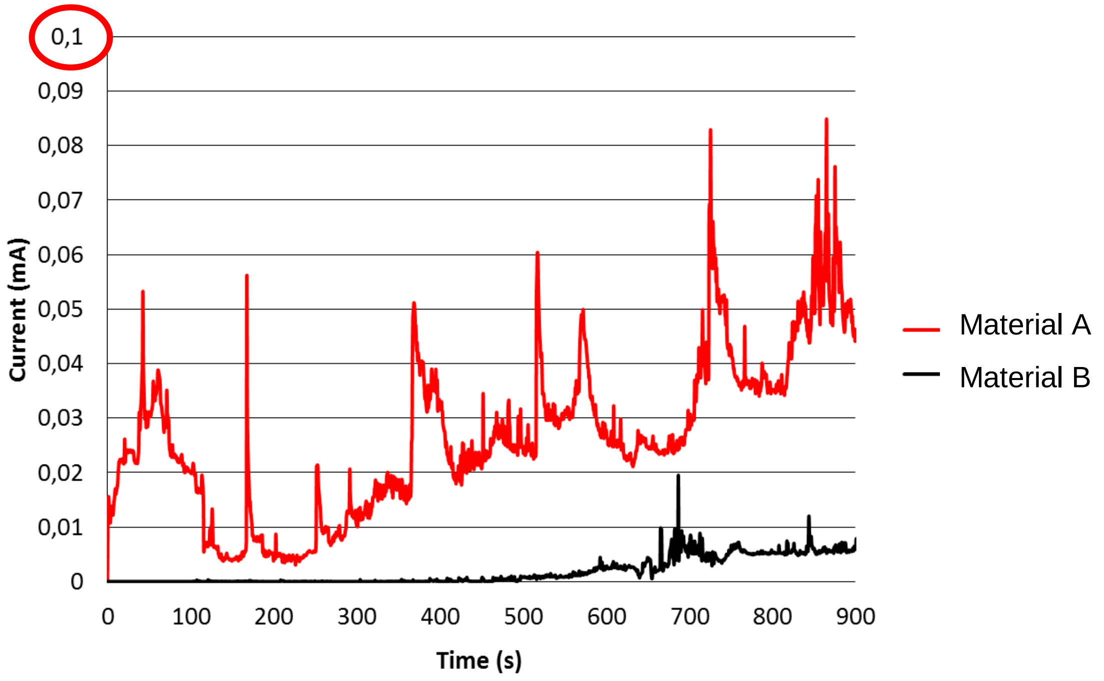
- 3µm waterproof (Material A) and 3µm sweatproof (Material B) coated PCB: no signs of corrosion after testing
- 4,7V





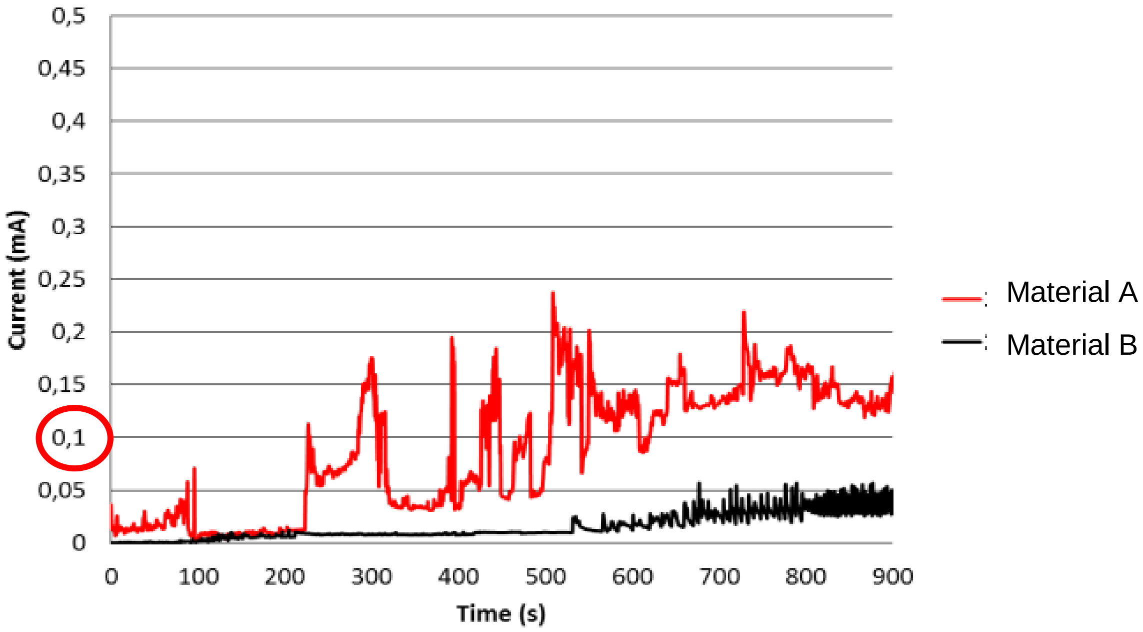
Submersion in Salt Water

- 3,57% NaCl
- 3µm waterproof (Material A) and 3µm sweatproof (Material B) coated PCB: no signs of corrosion after testing but Material B is more stable
- 4,7V



Submersion in Artificial Sweat

- pH 2,1; 2,5m% NH4Cl, 2,5m% lactic acid, 1m% acrylic acid
- 3µm waterproof (Material A) and 3µm sweatproof (Material B) coated PCB: Material B shows no signs of corrosion
- 4,7V



Contents

- Application history
- Low pressure plasma: an introduction
- Splashproofing of consumer electronics
- Water- and Sweatproofing
- High volume manufacturing case study
- Conclusions

500 liter Chamber

- Horizontal set-up with 3/5 trays

Case Study

- Product: earbuds
- SOP:
  - *Control PCBs: 3µm water- and sweatproof coating*
  - *Assembly*
  - *Optionally overcoat earbuds with ultra-thin splashproof coating*

Capacity

Product	Loading/Batch	Cycle Time (min)	Batches/ Day	Batches/ Year	Products/ Year
PCB	4 328	210	3	720	3 116 160
Over-coat	648	60	19	4 560	2 954 880

One 500 liter chamber can do about 1 500 000 earbuds per year

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Conclusions

- Low pressure plasma technology is fit for mass production
- Ultra-thin coatings provide splashproof protection to consumer electronics (IPX2-4), applied on components up to full devices
- Thin coatings provide waterproof to sweatproof protection to consumer electronics (IPX5-8), applied on component level for optimal protection
- Eco-friendly technology, low environmental footprint

Thank you for your attention!