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Through-hole plating with Polypyrrole in Printed Circuit Boards

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Abstract – *The goal of this paper is to investigate the use of polypyrrole (PPy) in the through-hole plating (PTH) stage of the Printed Circuit Boards (PCB) manufacturing process. The method includes: etching of FR4, in situ deposition of a thin film of PPy, resulting in a FR4/PPy electrode. Copper plated holes of FR4 multilayer PCB specimens were analyzed with the help of optical microscopy, Scanning Electron Microscopy (SEM) and EDS analysis. Tests on polypyrrole coated and copper plated holes also included conductivity and peel strength tests. Findings show that polypyrrole can be an equally good substitute for standard methods of hole-plating methods, like the ones based on palladium, carbon or graphite. Optical microscopy results indicate that a coherent copper layer is formed on the polypyrrole modified surface of the holes. The results of the SEM analysis help understand the mechanism of copper plating and show that copper nucleation is progressing with dendrite structures on the polypyrrole surface, following high conductivity paths. Improvements of the process of the specimens' pre-treatment, like holes desmearing and stirring of the polymer solution, were also analyzed.*

***Keywords**: PCB, PPy, PTH, plating through hole, conductive polymers*

I. Introduction

Printed Circuit Boards (PCB) are widely used for electronics applications. In microelectronics, PCBs are used to mechanically support and electrically connect electronic components using conductive pathways, or traces, etched from copper sheets laminated onto a non-conductive blank fiberglass substrate (the board). There are many types PCB substrate material, but by far the most common is a standard woven epoxy glass material known as FR4.

Figure 1: PCB specimen with the holes copper plated with the method developed by our team

The complexity of PCBs, vary from single-sided boards, where circuitry is found on only one side, to double-sided boards, to boards comprising several layers of circuitry. Connections between the two sides of a board and layer-to-layer connections are made with copper-plated through-holes (PTHs).

II. Problem Formulation

A PCB can consist of one single layer or of multiple layers of FR-4 epoxy, which inter-communicate with the help of copper plated holes (vias) between those layers. All multi-layer PCBs need further "through-hole plating" processing to allow the electrical communication between the different layers and a whole industry has evolved based on that need. Intrinsically conductive polymers, such as polyaniline and polypyrrole, have been used from the PCB industry in that direction for many years. The application of the conductive polymer in the PCB hole walls that allows their copper metallization at a later stage [1], is the main goal of our research.

II.1. Polypyrrole

Polypyrrole (PPy) (Figure 2) is one of the most widely used conductive polymers, due to its high chemical and physical stability, low toxicity of the monomer and its easy chemical or electrochemical synthesis, even in aqueous solutions [2], [3], [4]. This provides a serious advantage to methods based on polypyrrole, especially when taking into consideration the latest environmental concerns related to toxic materials used in the PCB production process [22]. PPy may be prepared by chemical or electrochemical oxidation.

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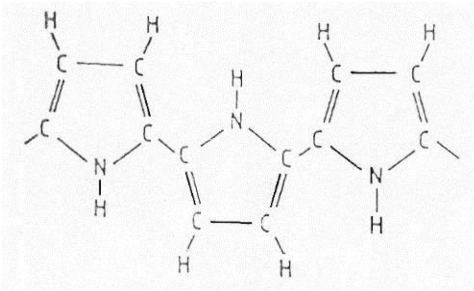

Figure 2: Polypyrrole (PPy)

It has been proven that by inserting doping anions like PTS (para-toluene-sulfonic acid) the conductivity of PPy can be increased up to 10^2 S/cm, [5], [6], [7].

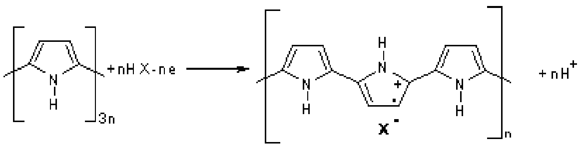

Figure 3: Doping mechanism of PPy

This highly conductive polypyrrole can be used to provide the intermediate layer that will allow the metallization of the initially non-conductive FR-4 walls of the PCBs.

II.2. Printed Circuit Boards

The manufacturing of Printed Circuit Boards (PCBs) is composed of many steps including the initial printing of the copper traces on the layers, the lamination of all the layers together, the drilling of holes and, finally, the copper plating of these holes in order to allow the electrical communication of the layers between them. One of the main materials used for PCB manufacturing is an epoxy material called FR-4 (*Fire Retardant-Grade 4*). FR-4 can be Al or Br based. The specimens used by our team were Br based as indicated by the EDS analysis.

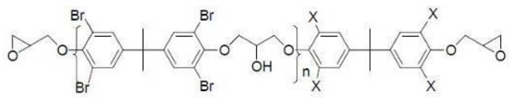

Figure 4: Br-based FR-4 structure

The molecule of Br-based FR4 material is depicted in Figure 4. Our experiments have shown that polypyrrole can be applied directly on the FR-4 epoxy as part of the PCB manufacturing process.

II.3. Through-hole plating (PTH)

The through-hole plating stage includes two steps: the application of a precoat on the hole walls – so as to make them conductive – and the copper metallization of those walls. The copper metallization is applied with electroplating. The minimum diameter of through holes in the industry will decrease on average from 0.3 mm to 0.2 mm [17].

Two of the most popular precoats are graphite and conductive polymers like polypyrrole (our method, which will be analyzed below). Hybrid methods include the electroless creation of an initial thin copper layer on FR-4 and the subsequent copper electroplating of the PCB vias, until the required thickness of the copper layer is reached. Other technologies for PTH include the use of ion tracks to facilitate the electrical communication between the layers [21].

Chemical or laser-induced [18] etching of the hole walls is applied before the process.

III. Problem Solution

The aim of the present study is to investigate the application of polypyrrole (PPy) as a conductive in situ precoat for the metallization of PCB holes. Several variables of the process at a laboratory level were studied.

In particular, we studied two methods of applying the conductive PPy precoat on the PCB FR4 hole walls, in order to make them conductive. The first method is based on solution immersion: the FR4 specimen is immersed in the oxidant solution and the monomer solution is added afterwards – thus resulting in the in situ polymerization of pyrrole into PPy on the hole walls. The second method is based on the simultaneous spraying of the pyrrole monomer and the required oxidant directly on the PCB hole walls.

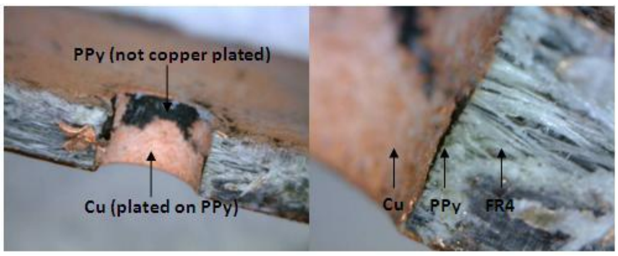

Figure 5: Copper plated PCB hole with our method

Both of our methods result in the modification of the substrate surface with polypyrrole (creation of FR4/PPy electrode) and the subsequent electroplating of the specimens to a FR4/PPy/Cu electrode.

The advantage of the method based on spraying is that it is more suitable for automated manufacturing processes. The disadvantage of the spraying method is that is does not offer the same quality in the copper plating of small vias, when compared to the immersion method.

We analyzed the results with optical microscopy and with SEM/EDS analysis. The peel strength of copper coating (Cu) on the polypyrrole-modified FR4, was measured according to ASTM-B-193-02 specification. Preliminary tests of the conductivity achieved with FR4/PPy electrodes were also conducted.

III.1. Our method

As part of our method, firstly PCB specimens with holes (2.5 x 2.5 cm) were etched by immersion for 1 min in a firmly agitated aqueous solution containing 8% pv $(NH_4)_2S_2O_8$. Ammonium persulfate acts as an oxidant in the polymerization of pyrrole. PPy is polymerized on the FR4 surface, from an appropriate optimized solution that contains 3.6% pv. pyrrole and 4.4% pv. PTS that acts as a dopant [8]. Thus, a new electrode is formed that can be electroplated.

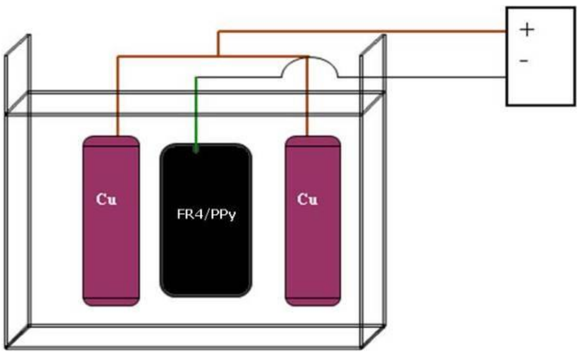

Figure 6: The electrolytic cell used for copper plating

The FR4/PPy electrode has been electroplated using the electrolytic cell that contained a copper ion bath. The composition of the copper deposition bath was: 150 g/L $CuSO_4*5H_2O$, 50 g/L H_2SO_4, 50 g/L CH_3CH_2OH (EtOH). Copper was deposited onto FR4/PPy surface resulting in the formation of a FR4/PPy/Cu sample.

With the spraying method, polypyrrole is formed by in situ polymerization at a single stage during which the pyrrole and the oxidant solution are sprayed simultaneously in the holes.

IV. Specimen Analysis

The walls of the holes of the specimens were analyzed with the help of optical microscopy and with the help of SEM. Optical microscopy photos of specimens with PPy deposited on FR4 were taken, along with photos of specimens copper plated. We cut cross-sections of the holes and applied magnifications of x100 up to x500 to examine them. The results of the analysis show that the layer of polypyrrole allows the full copper plating of the holes' walls.

Microscopy photos of specimens with polypyrrole deposited on the hole walls are depicted in the following figures (Figure 7, Figure 8).

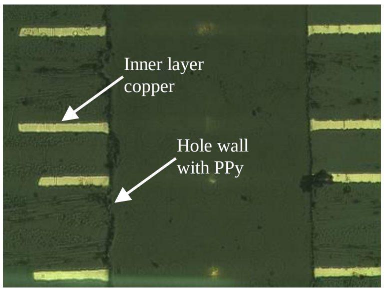

Figure 7: Cross section of PCB hole walls with PPy [x100]

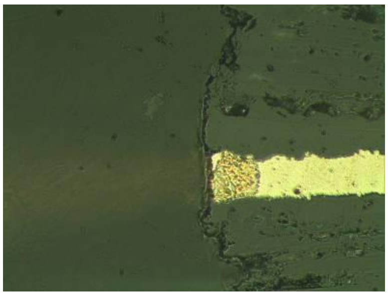

Figure 8: Cross section of PCB hole walls with 2.73 μm width of PPy [x500]

The examination of those specimens with the hole walls covered only with polypyrrole (at a stage before the final copper plating of the holes) showed that polypyrrole was deposited on the whole length of the hole walls in the form of a thin film with thickness ranging from 2.5 μm to 5.5 μm.

Further analysis was performed on copper plated specimens. Microscopy photos of specimens' copper plated hole walls are depicted in the following figures. The copper layer did not present any gaps and was coherent.

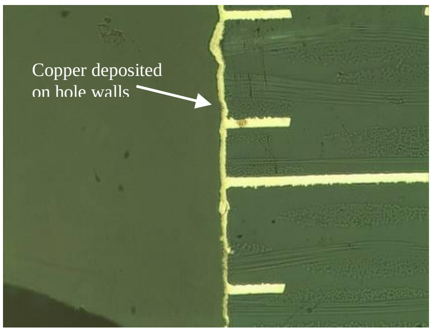

Figure 9: Cross section of copper plated hole walls of PCB specimen. Copper width measured to 12.3 μm [x100]

The analysis also shows that there is sufficient connection between the copper layer deposited on the via walls and the copper of the inside layers. This is verified by the SEM analysis of inner-copper and deposited-copper interconnection (Figure 10).

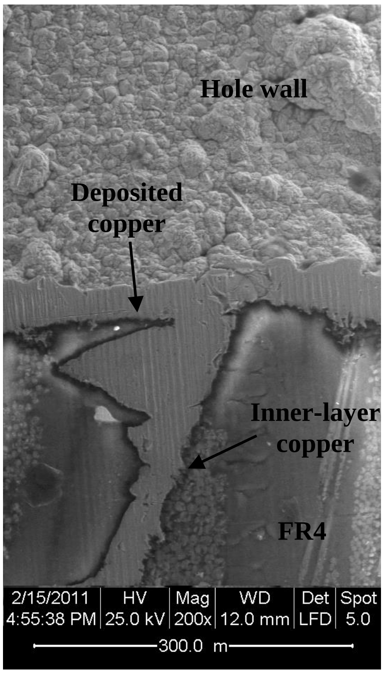

Figure 10: Cross section of the connection point between inner PCB layer copper and copper deposited on hole walls [x200]

A possible explanation is that the polypyrrole is embedded into the copper layer deposited at a later stage. The diffusion of copper ions into the polypyrrole layer has been observed in previous research conducted by our team. [2] This is also suggested by the fact that the current density during the electroplating reaches a plateu, as indicated in the following schema.

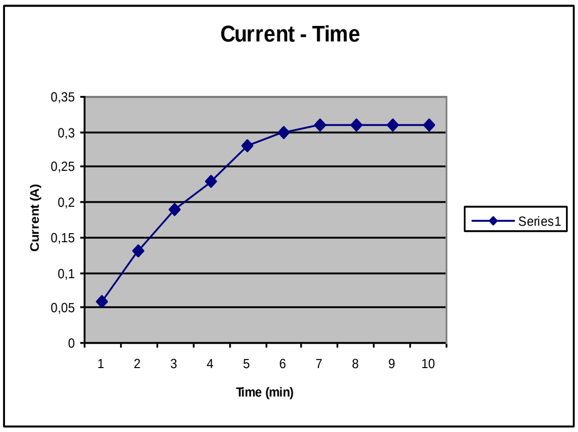

Figure 11: Evolution of current density vs. time during electrodeposition

One of the advantages of our method is the fact that it is performed in one phase instead of two phases (electroless and electroplating). In the latter methods the copper deposited first (in the electroless stage) is not well connected to the copper deposited at the electroplating stage, thus resulting in adhesion problems. [9]

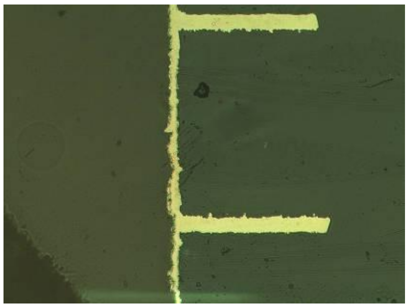

Figure 12: Cross section of copper plated walls of PCB with 12.3 μm width [x200]

Due to the geometry of the electrochemical cell used for copper plating, the copper front starts propagating from the hole walls towards the inner side of the holes. This results in the copper layer being more thick near the hole entrance than near the center of the hole (Figure 11). In the specimens examined, the copper layer thickness ranged from 8-12 μm from the hole entrance to the inner hole walls.

V. COPPER DEPOSITION MECHANISM

PCB FR4 Specimens with copper plated holes were analyzed with the SEM/EDS method. Two types of specimens were analyzed:

- Specimens copper plated with no stirring applied during the electroplating process
- Specimens copper plated with stirring applied during the electroplating process

Results depicted the uniformity of the polypyrrole layer and show that during the electroplating process the copper front propagates with different mechanism depending on if stirring is applied during the process.

A. Specimens copper plated with no stirring

If no stirring is applied the copper front propagates via high conductivity paths, forming dendrite structures on the polypyrrole surface as suggested by the below figures (Figure 12, Figure 13).

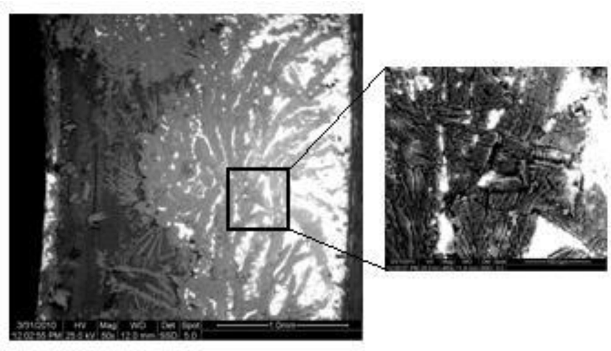

Figure 13: SEM photo of a copper plated PCB hole with our method taken before the plating was completed (copper front is propagating from right to left)

The existence or the creation of high conductivity paths on the FR4 hole walls, affects the process of copper deposition [10], as these dendrite structures indicate.

Other researchers indicate that the copper deposition begins from the imperfections of the surface. [11] The SEM images indeed show that the new copper nucleus are forming in flaws of the inner hole surface (e.g. points where the glass fibers are exposed).

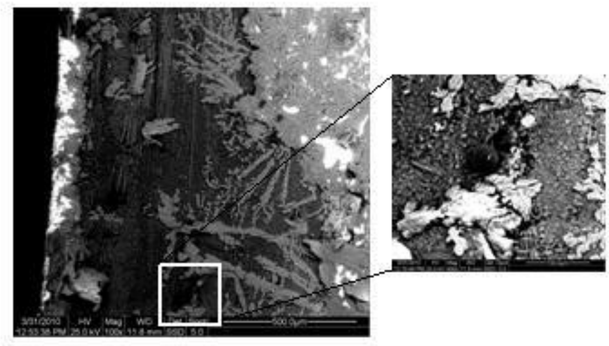

Figure 14: Detail of the PCB hole walls of Figure 12.

The EDS analysis of areas covered by polypyrrole and of areas copper plated, show the elements synthesis of areas covered with polypyrrole and areas covered with copper.

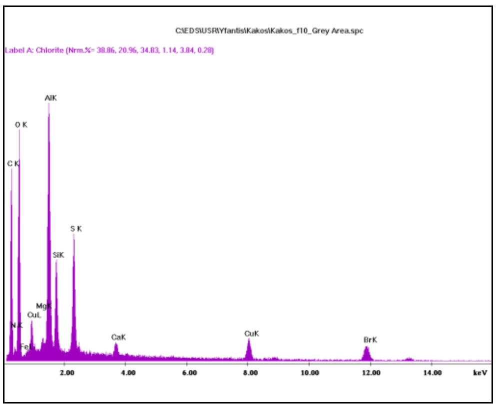

Figure 15: EDS analysis of area covered with polypyrrole, with no copper present

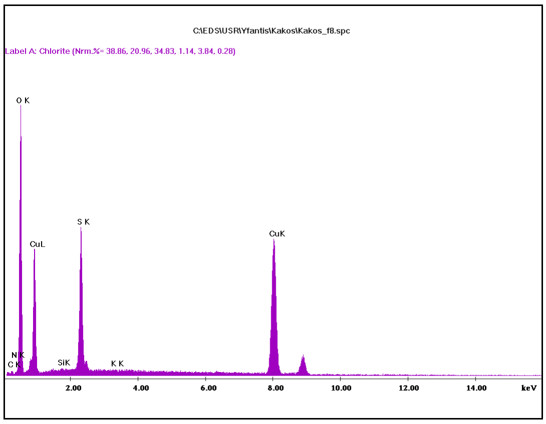

Figure 16: EDS analysis of area covered by copper

B. Specimens copper plated with stirring

The formation of copper nuclei on the hole walls has been visualized in our findings (Fig. 17). The copper front in specimens copper plated with stirring applied during the process, propagates through a nucleation mechanism, as indicated by the figures that follow.

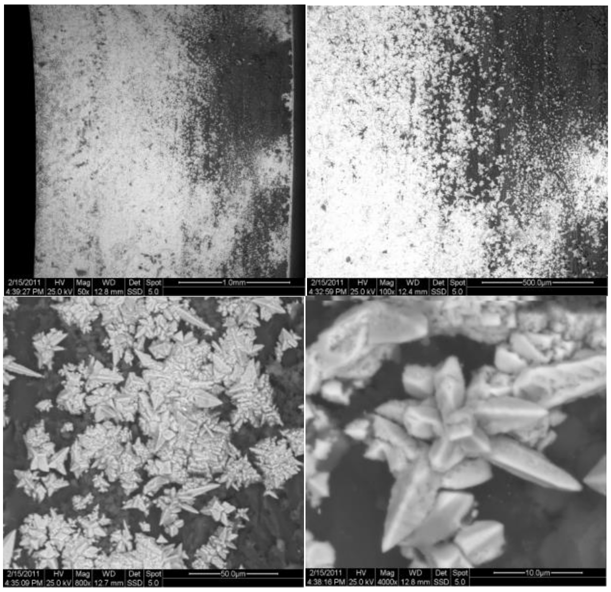

Figure 17: Formation of copper nuclei during copper plating of FR/PPy surface. X50, x100, x800, x4000 magnifications

It is evident that during the electroplating of the specimens with stirring applied, the copper plating progresses uniformly via copper nucleus formed on the PPy surface.

Other researchers propose that nucleus of CuO or Cu_2O are initially created. Those nucleus are then transformed into copper crystals. [10]

From previous research we conducted the copper deposition mechanism is controlled by diffusion [12]. The current plateau to which the process reaches during the electroplating can be attributed to the copper ions diffusion (from the plating bath to the FR4/PPy surface, via an intermediate layer).

These results are in agreement with the results of other researches concerning the copper plating mechanism. Scharifker and Hills, proposed a 3-dimentional nucleation mechanism which is also controlled by diffusion [11]. The deposition of copper is conducted with a 3-dimentional nucleation mechanism as proposed by other researchers as well [13], [14]. Diffusion plays a key role in this mechanism also [14].

VI. Peel strength and Conductivity

Our team examined the peel strength of the polypyrrole layer on the FR-4 surface and the peel strength of the copper layer on the PPy surface.

Initial analysis showed that polypyrrole has more adhesion to copper than to FR4. Tests failure was due to the low adhesion of PPy to FR4, than due to low adhesion of PPy to copper.

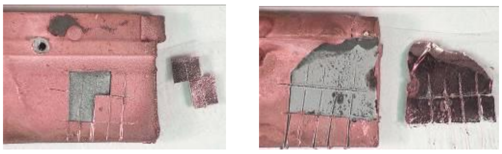

Figure 18: Peel strength test of PCB surface

In particular, the adhesion of copper deposit was tested according to the ASTM D 3359, method B (*"Cross-Cut Tape Test")*. Two specimens were tested. In the first specimen tested 42% of the deposit was peeled off while in the second one 66% was peeled off. Photos of the tested specimens are shown in the figure above.

From the experiments we conducted, we concluded that the drying of polypyrrole immediately after its deposition is critical for the PPy layer to connect well to the FR4 surface for the success of the copper plating. The same applies for the graphite-based method, where the graphite layer must be dried very well so as to adhere to the FR4 substrate, before the copper plating stage begins [13].

Removing the air from the holes before electroplating also increases the quality of the copper deposited, resulting in a more uniform layer. This comes in accordance with findings from others teams [15] [17].

The conductivity of the FR4/PPy electrodes formed during the process was investigated. Initial measurements showed that the resistance of a hole with 1 mm diameter and 1 mm length, was about 0.650-0.750 MΩhm.

VII. Conclusions and Results Discussion

Within the limitations of this study, the following conclusions can be drawn:

Polypyrrole is deposited on all the inner surface of the PCB hole walls.

The FR4/PPy electrode has sufficient conductivity to allow the copper plating of the PCB vias. Resistance is about 0.700 MΩhm for a 1x1 mm hole.

This result can be correlated to reported results by A.J. Cobley et al [23] , in which virtually no electroplating penetration into the through hole was obtained when the through holes were processed using mechanically stirred copper nanoparticles to help the copper electrodeposition at a later stage.

Drying of the polypyrrole immediately after its deposition on FR4 hole walls is critical to reach good adhesion levels.

The copper layer resulting from our method is coherent and has sufficient adherence to FR4. Polypyrrole deposited on the intermediate layers of multilayer PCBs does not create cohesion problems between the inner layer copper and the copper deposited on the hole walls, because the copper deposited is embedded in the polypyrrole structure.

When no stirring is applied, copper is deposited on the PPy film following high conductivity paths thus resulting in dendritic structures. When stirring is applied, copper is deposited via a more homogeneous 3-D nucleation mechanism.

Results indicate that the deposition mechanism is controlled by diffusion, something in accordance with results from other teams [19], who have also observed the current density reaching a limit at some point in the copper plating process providing indications that the mass transfer of Cu^{2+} is controlling the reductive reaction [15]. Chien-Hung Chen et al have also suggested that Therefore, the adsorption/consumption/diffusion model is the only mechanism that could explain the deposition mode [16].

The observed crystalline size of deposited copper (see Fig. 17) of about 12 nm is in accordance with the average crystalline size reported by Ralf Brüning et al [20].

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