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## Electro-deposition as a repair method for embedded metal grids



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### ABSTRACT

A method is presented to self-repair cracks in embedded silver grid structures used in large area organic electronics. The repair procedure is based on electro-deposition, incited by the application of a moderate DC voltage across the crack. During this process the organic anode that is in direct electrical contact with the silver grid, functions as an appropriate medium for ion migration. Restoration of conductivity is achieved by the formation of dendritic metal structures that connect the cathodic to the anodic side of the crack. The metal dendrites decrease the gap resistance by one order of magnitude. Subsequently, another three orders of magnitude are gained upon sintering the dendrites using a high voltage pulse, yielding restored conductance levels nearly within one order of magnitude difference from native track conductance.

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### 1. Introduction

In order to suppress material cost in the manufacture of large area thin film flexible organic electronics devices, such as (solution-processed) organic light-emitting diodes (OLEDs) and organic solar cells (OSCs), the traditionally used anode material indium tin oxide is replaced by a high conductive grade of the organic *p*-type semiconductor poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) [1–3]. In typical device architectures the PEDOT:PSS anode is in contact with a metallic grid structure (see Fig. 1A), either for voltage control (*i.e.* in case of OLEDs) or current collection purposes (*i.e.* in case of OSCs) [2, 4, 5]. The grid itself is usually applied by a printing method [6, 7] followed by a curing or sintering step. To date, the metal most widely used for the fabrication of such grids is silver (Ag) [8], owing to its low resistivity, compatibility with printing methods [9–11] and reasonable air stability. The grid lines can typically be up to a micron high, *i.e.* considerably exceeding the thickness of an organic layer (Fig. 1 is not drawn to scale). As a result, the flexural strength of the grid lines is compromised, imparting the risk of crack formation if applied in flexible or stretchable device architectures [10]. An increase in crack density leads to compromised device performance and ultimately complete failure.

Besides the above-mentioned properties advantageous to the fabrication of metal grids, silver is also known to exhibit electro-deposition in the

presence of an electric field [12]. In the manufacture of integrated circuits this phenomenon is considered a severe drawback as it leads to the formation of undesired metallic structures giving rise to parasitic current pathways and/or short-circuiting [12, 13]. Besides the presence of an electric field, another prerequisite for electro-deposition is the presence of a condensed medium that accommodates silver cations that are oxidatively generated at sites at sufficiently high anodic potential. The cations migrate towards sites at cathodic potential where they become reduced and deposit in the zero-valent state. As under those conditions the deposition process is diffusion/migration limited, the metal structures that consequently grow in the opposite direction (*i.e.* from cathode to anode) typically have a dendritic morphology [12].

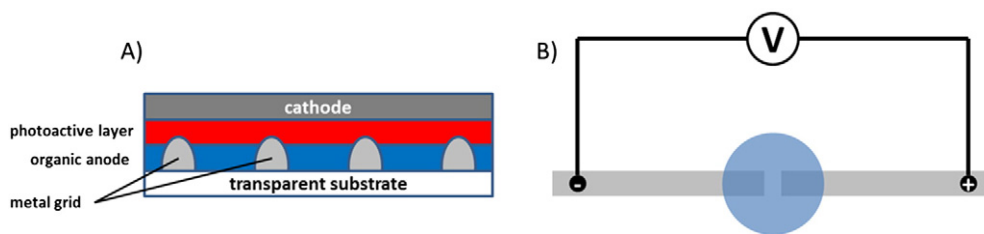
In this work we demonstrate that electro-deposition of silver can advantageously be used to repair cracks in printed silver grid lines, restoring metallic conductivity. We show furthermore that PEDOT:PSS, being a polyelectrolyte usually containing residual humidity, can act as a suitable medium for the accommodation and transport of cations. To investigate whether the dendritic growth is affected by the highly acidic nature of PEDOT:PSS and by the semiconducting nature of the PEDOT fraction, we also tested poly(styrene sulfonic acid) ( $\text{PSS}^- \text{H}^+$ ), as well as its sodium salt ( $\text{PSS}^- \text{Na}^+$ ) as alternative media to systematically eliminate the effects of conductivity and acidity.

### 2. Experimental details

Interrupted silver lines ( $\sim 3$  cm long,  $\sim 1000$   $\mu\text{m}$  wide and  $\sim 10$   $\mu\text{m}$  high) are produced by stencil printing a particulate-based silver ink

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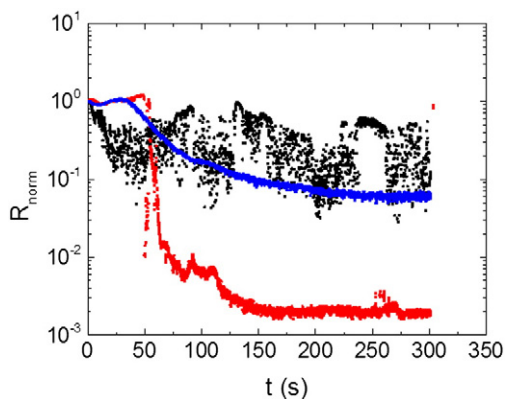


**Fig. 1.** A) Schematic representation of a cross-section of an OLED or OSC containing an organic anode (such as PEDOT:PSS) and a metal grid structure for voltage control or current collection purposes. B) Schematic representation of the test set-up used in the present work: a three cm long silver track (grey) containing a 200  $\mu\text{m}$  wide gap is screen-printed, after which the gap region is covered by a drop-cast polyelectrolyte film (blue); a DC voltage is then applied across the gap to incite electro-deposition.

(Silver Nano-Past DPG-NO, Advanced Nano Products) onto poly(ethylene terephthalate) substrates with a thickness of 100  $\mu\text{m}$ , followed by a photonic sintering method, the details of which having been published elsewhere [14]. The width of the interruption, which simulates an actual crack, is controlled at about 200  $\mu\text{m}$ . Polyelectrolyte medium (*i.e.* PEDOT:PSS,  $\text{PSS}^- \text{H}^+$ , or  $\text{PSS}^- \text{Na}^+$ ) is applied by casting a 1  $\mu\text{L}$  droplet of a 0.75 wt.% aqueous solution on top of the gap, covering both ends of the printed line segments (see Fig. 1B). The films are dried at 130  $^\circ\text{C}$  and subsequently equilibrated at 20  $^\circ\text{C}$ /50% relative humidity (RH). The resistance of the interrupted tracks is measured in real-time whilst inciting electrodeposition inside the gap by application of a 5 V potential using a Keithley 2400 SMU.

### 3. Results and discussion

Instead of considering complex grid structures in our experiments we study crack repair using a model system consisting of deliberately interrupted printed silver tracks (see [Experimental details](#) section for details concerning the fabrication of the tracks). Fig. 2, in which we plot the resistance (scaled by the initial value) as a function of time, indeed shows a healing effect for all three polyelectrolytes, though accomplished *via* a markedly different behaviour. Interestingly, in case of PEDOT:PSS the gap resistance decreases gradually towards a stable saturation value, whereas a “switching” behaviour characterized by abrupt changes is observed for  $\text{PSS}^- \text{Na}^+$  and  $\text{PSS}^- \text{H}^+$ . The largest changes in resistance are typically observed for  $\text{PSS}^- \text{Na}^+$ . Although there is a significant sample-to-sample variation in the absolute values of the measured resistance, the shapes of the curves are highly reproducible and likely relate to (differences in) the morphology of dendritic or filamentary metal structures formed inside the gap.

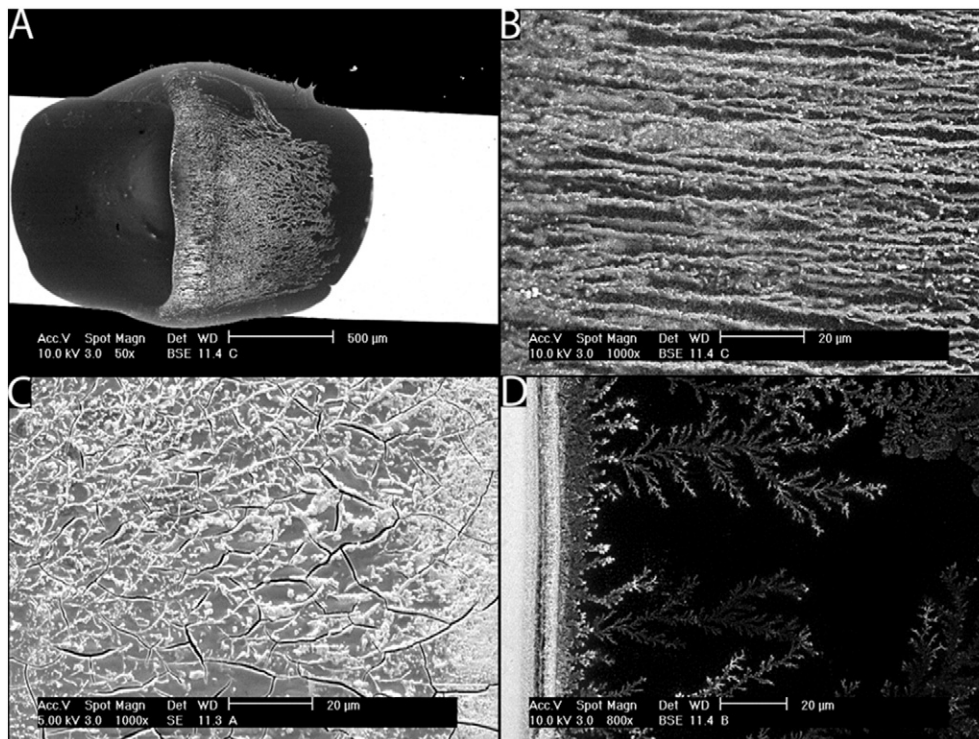


**Fig. 2.** Normalised resistance ( $R_{\text{norm}}$ ) as function of time ( $t$ ) for dendritic growth in different polyelectrolytes; blue: PEDOT:PSS; black:  $\text{PSS}^- \text{H}^+$ ; red:  $\text{PSS}^- \text{Na}^+$ .

We used scanning electron microscopy (SEM) to study the morphology of these structures (Fig. 3). Fig. 3A shows an exemplary low-magnification image of the result after a 300 s application of a 5 V potential. The white regions represent the cathodic (left) and anodic (right) segments of the interrupted silver track. The dark roundish area represents the drop-cast polymer film (in this case PEDOT:PSS), below which the  $\sim 200$   $\mu\text{m}$  wide gap can be discerned. Across the gap one indeed clearly distinguishes the dendritic metal pattern that as a result of electro-deposition has grown in the direction from the cathode to the anode. Strikingly, in this case the dendrites have not stopped growing upon reaching the anodic side of the gap, but rather have continued to grow over the anode. This suggests that despite the establishment of electrical contact, the electric field between the dendritic network (*i.e.* at cathodic potential) and the anodic line segment is to some extent retained, which explains the rather modest decrease in gap resistance observed for PEDOT:PSS. The same behaviour is observed when  $\text{PSS}^- \text{H}^+$  is used as migration medium (data not shown), but *not* for the neutral  $\text{PSS}^- \text{Na}^+$ , for which the development of the dendritic morphology rather remains contained to the gap itself, at least on the timescale of the experiment.

Higher magnification images (Fig. 3B, C, and D) indeed reveal considerable morphological differences between structures grown in different media, as already hinted towards by the different shapes of the resistance *vs* time curves. In case of PEDOT:PSS (Fig. 3B) parallel filaments form that seem to follow the electric field lines in the gap. In contrast,  $\text{PSS}^- \text{H}^+$  (Fig. 3C) gives rise to a highly branched morphology, whereas  $\text{PSS}^- \text{Na}^+$  (Fig. 3D) yields tree-like structures. With respect to  $\text{PSS}^- \text{H}^+$  it must be noted that it is not inconceivable that the development of the dendritic morphology is influenced by the somewhat unfortunate formation of cracks in the dry film (Fig. 3C). A clear distinction can be made between the dendritic morphologies obtained for the neutral  $\text{PSS}^- \text{Na}^+$  and the two acidic  $\text{PSS}^- \text{H}^+$ -based media in the sense that in case of the former the spatial distribution of the dendrite material is much less isotropic. In other words, the ratio between the typical distance between dendritic sections and the total width of the silver track is very small for PEDOT:PSS and  $\text{PSS}^- \text{H}^+$  but significantly higher for  $\text{PSS}^- \text{Na}^+$ .

Combining the results presented above, we propose the following qualitative explanation for the observed differences in the resistance *vs* time curves. The decrease in resistivity clearly evidences that the dendrites resulting from electro-deposition indeed establish electrical contact between the two line segments. A switch back to high resistance at any moment in time can be explained by the notion that the dendritic filaments are thin and therefore prone to fuse upon suddenly accommodating an electrical current. If the dendrites grow sufficiently fast and in a spatially isotropic fashion, perpetual connecting and fusing eventually reaches steady state, giving rise to a stable resistance value, as observed for PEDOT:PSS. Contrarily, in case of slow and/or anisotropic growth, individual reconnecting and fusing events are observed. The fact that for  $\text{PSS}^- \text{Na}^+$  the measured resistance switches back and forth across a wide range (*i.e.* several orders of magnitude) but with long time



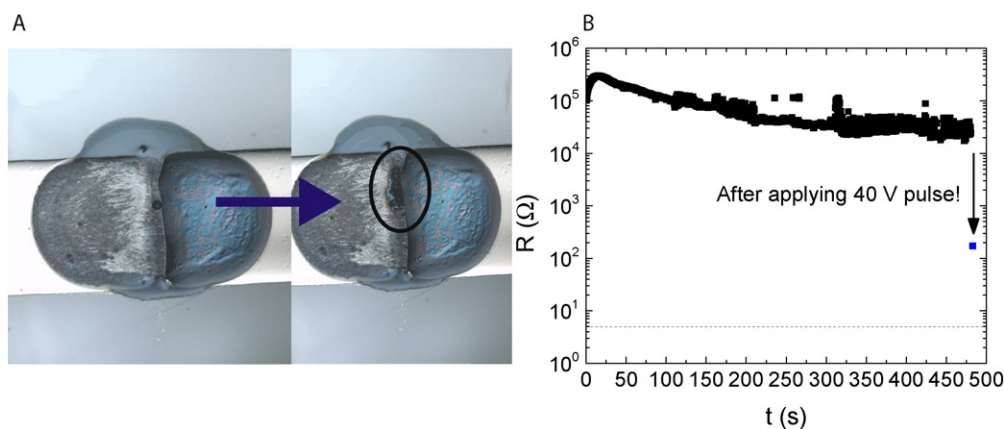
**Fig. 3.** Scanning electron microscope (SEM) images of silver dendrites grown as a result of electro-deposition in A, B) PEDOT:PSS; C) PSS<sup>-</sup>H<sup>+</sup>; D) PSS<sup>-</sup>Na<sup>+</sup>.

intervals suggests that the dendrites connecting to the anode are (on average) relatively robust in comparison to, for instance, the ones grown in PSS<sup>-</sup>H<sup>+</sup>, for which the resistance switches across a much smaller range but at a significantly higher frequency.

As mentioned in the introduction, the decision to involve PSS<sup>-</sup>H<sup>+</sup> and PSS<sup>-</sup>Na<sup>+</sup> in this study, despite the fact that these polyelectrolytes are irrelevant to application as organic anodes, is to gain insight in the effect of acidity and conductivity of the migration medium on dendritic growth. As the electro-deposition rate is known to be strongly dependent on the humidity of the medium [13,15] we confirmed that all three polyelectrolytes have similar hygroscopicity before making conclusions on acidity-related effects. As we indeed obtain very similar values for the equilibrium water concentration (using Karl-Fischer titration) at 20 °C/50% RH, i.e. 15.63%, 15.61% and 11.69% for PEDOT:PSS, PSS<sup>-</sup>H<sup>+</sup>, and PSS<sup>-</sup>Na<sup>+</sup>, respectively, we ascribe the much more pronounced

dendritic growth observed for PEDOT:PSS and PSS<sup>-</sup>H<sup>+</sup>, in comparison to the neutral PSS<sup>-</sup>Na<sup>+</sup>, to an increased production of cations *via* chemical corrosion of silver. Unfortunately, the influence of the conductive nature of the PEDOT fraction is momentarily not straightforwardly extracted from our experimental results. More research concerning this point is currently on-going.

For all media partial repair of the simulated crack is achieved by electro-deposition, evidenced by the decrease in gap resistance. For the relevant organic anode material PEDOT:PSS, however, the recovery is only modest (about one order of magnitude) and likely insufficient to allow for fully restored operation of a thin film device. For this reason we have extended the repair procedure with the application of a 10 ms high voltage (40 V) pulse after allowing for the formation of a significant amount of dendritic silver inside the gap at low voltage (5 V). As indicated by Fig. 4A, the dendritic structures consequently



**Fig. 4.** A) Screen printed silver track (white regions) with a 200 μm wide interruption covered with a drop cast film of PEDOT:PSS (blue-ish region) and exposed to 5 V for ~470 s followed by a 10 ms pulse at 40 V; the left and right hand images in (A) represent the situation before and after application of the 40 V pulse; B) resistance plotted as function of time, real-time recorded prior to (black squares) and after (blue square) application of the 40 V pulse; the dashed black line represents the resistance of the native silver track.

melt to yield bulky, drop-like metallic features. Melting likely occurs via local heating due to the strongly increased current density during the pulse. Fig. 4B shows that these features are much better capable of accommodating the current than the native dendrites: upon application of the 40 V pulse another three orders of magnitude gain in gap conductance is obtained down to a resistance of about 100  $\Omega$ , which is nearly within an order of magnitude from the resistance of the pristine silver track.

#### 4. Conclusions

In conclusion, we have shown that electro-deposition of silver can favourably be employed to repair cracks in silver metal structures of interest to thin film flexible organic electronics. The repair process is demonstrated by means of a model system comprising a printed silver track containing an interruption simulating a real life crack. Electro-deposition inside the crack that is covered with polyelectrolyte is observed upon application of a moderate field across the two ends of the interrupted track. Conductivity is partially restored due to the growth of dendritic as a result of subsequent oxidation/formation and reduction/deposition of silver. It is shown that the dendrite morphology is dependent on the polyelectrolyte. A considerable further drop in gap resistance is achieved by application of a high voltage pulse after significant prior dendrite growth at low voltage. The pulse effectively melts the dendritic network, giving bulky silver features capable of accommodating considerable electrical currents without fusing. Hence, a healing protocol is obtained that yields repaired metal tracks having conductance levels nearly within an order of magnitude from those of pristine counterparts.

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