



## Controlled Ag release from electrically conductive coating systems

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### ABSTRACT

Nowadays, silver (Ag) coatings find widespread use in medical textiles, e.g. wound bandages, mainly due to their antibacterial properties related to the Ag ion release in aqueous media. Moreover, Ag-coated fibers offer excellent electrical properties, allowing their use for sensing applications such as electrocardiography (ECG) belts. Due to the potential cytotoxicity of Ag, electrically conductive coating systems need to be developed with reduced and time-controlled Ag release.

In this study, pure silver was continuously deposited onto a polyester (PET) fiber to optimize electrical conductivity for ECG application. The pure silver coated fibers, however, showed the typical initial burst release of Ag ions when immersed in an aqueous environment locally yielding cytotoxic conditions, i.e. high Ag ion concentrations. While the ion release can be favourable for antibacterial properties, it needs to be limited for medical devices. A diffusion barrier is thus required, while maintaining the electrical conductivity. Thus, different plasma polymer top coatings were applied onto the Ag-coated fibers using a continuous deposition process. The functional plasma polymerized films (a-C:H and a-C:H:O) were compared with an ultrathin titanium oxide layer (as recently investigated) regarding electrical properties and silver release. Ag release measurements demonstrated that an efficient control over the release properties (initial burst and long-term release) was achieved depending on the hydrophobicity and thickness of the plasma polymer films.

### 1. Introduction

Bacterial colonization and infection are of great concern in medicine, and also in daily products exposed to water or humidity. The antibacterial action of silver is used in numerous consumer products and medical devices. Metallic silver, silver salts, and also silver nanoparticles are commonly used for this purpose [1]. The state of research on the effect of silver on bacteria, cells, and higher organisms has already been well summarized, e.g., by Chernousova and Epple [2].

Antibacterial effects in general should be based on time-controlled release of substances to achieve a good balance between antibacterial activity and biocompatibility [3,4]. Silver particles are thus embedded within a matrix or are covered with a top-coating acting as a diffusion barrier [5]. Both methods restrict water diffusion to the silver reservoir as well as leaching of Ag ions into the solution. Several studies carried out over the past decades proposed the embedding of Ag ions or nanoparticles in various organic or inorganic matrixes in order to gain a better control over release properties [6]. For example, silver ions were embedded in Si-based sol-gel [7] or in spin-coated PMMA films [8], and silver nanoparticles were inserted in electrospun PMMA [9], PVA [10] or gelatin fibers [11]. More recently, plasma-based coatings, such as oxygen-containing [12] or nitrogen-containing [13] plasma polymer

films as well as fluorocarbon, hydrocarbon and SiO<sub>2</sub>-based plasma coatings [14,15] were used as matrix for silver particles.

The silver release from a surface depends on the exposed area used in the application and on the availability of the deposited silver. Especially fibrous substrates are suitable materials for long-time antibacterial effects as they have a large surface area, able to yield high Ag ion concentrations by leaching from the Ag-coated areas. Ag ions provide a broad activity against bacteria. High Ag ion concentrations (exceeding about 1 µg ml<sup>-1</sup>) as they might locally occur by the so-called initial burst release, however, are known to be cytotoxic [4]. Such conditions are not suitable, e.g., for applications related to sensing and measurement of electrical body vital signals, such as electrocardiography (ECG) [16].

For textile electrodes a certain electrical conductivity of the applied coating system is essential. Silver shows a high conductivity and ductile behavior suitable for electrical application on fibrous substrates [17]. Due to its corrosion resistance and its ability to passivate a silver layer [18], titanium top-coatings were deposited onto silver-coated fibers. The obtained Ag/Ti metal layer systems had been studied towards their silver release, showing strong reduction of Ag release and high potential for ECG applications [16]. For measurements with dry skin an additional water environment dosed through a membrane can reduce the

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skin electrode contact resistance and improve the obtained ECG signal [19].

The current study aims to control the silver release from an Ag-coated fiber covered with hydrophobic a-C:H or hydrophilic a-C:H:O plasma polymer films to investigate functional diffusion barrier coatings. As the a-C:H:O plasma polymer matrix is rich in oxygen containing functional groups, noticeable water permeation can be expected. Besides effective control of the Ag ion release, the demanded electrical conductivity and contact resistance can be maintained over a rather wide range regarding the top coating thickness. Results obtained for the Ag-coated fibers with a-C:H and a-C:H:O top-layers are compared to previously observed results for titanium-passivated Ag fibers [16], in order to study their potential as surface functionalization of electrically conductive fibers.

## 2. Materials and methods

### 2.1. Substrate and surface area

Polyester (PET) fibers 150f48 comprising a silver coating with different amounts of deposited silver (Serge Ferarri Tersuisse SA, Switzerland) were used in this study. The nomenclature 150f48 indicates a fiber weight (fineness) of  $15 \text{ mg m}^{-1}$  (150 dtex) for the polyester fiber (with a density of  $1.37 \text{ g cm}^{-3}$ ) made of 48 filaments. For comparison also a PET 167f134 (polyester  $16.7 \text{ mg m}^{-1}$  and 134 filaments) Ag-coated fiber material was considered. The specific fiber surface area  $A$  (per fiber length) can be calculated from Eq. (1):

$$A = 2\sqrt{\frac{m \pi F}{l \delta}} \quad (1)$$

where  $m$  is the mass (g),  $\delta$  the density ( $\text{g cm}^{-3}$ ),  $l$  the length (cm) and  $F$  the number of filaments of the fiber.

### 2.2. Silver and titanium coatings and film thickness determination

Silver and titanium layers were coated on the fibers by magnetron sputtering according to the protocol as reported in [16,20]. The mass of the applied silver and titanium coatings were analyzed by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) Optima 3000, Perkin Elmer. Silver-coated fibers of four meter length each were dissolved in concentrated nitric acid and diluted with water. The Ag-containing solution was then introduced into the ICP-OES and optically analyzed (Ag lines at 328.068 nm and 338.289 nm). The calibration was performed using an external silver standard solution of  $1 \text{ g l}^{-1}$ . A recovery rate between 98 and 101% was obtained. Silver detection limit is  $\leq 0.075 \mu\text{g} \cdot \text{m}^{-1}$ . Titanium coatings were analyzed with the same method using the protocol as described in [16].

The theoretical (average) film thickness  $d_f$  of a homogeneous film over all 48 filaments was calculated from the measured mass of the deposited metal film. The Ag coating was deposited with either  $1.7 \text{ mg m}^{-1}$  (deposited Ag mass per fiber length) resulting in 62 nm Ag thickness (calculated average) or  $4.5 \text{ mg m}^{-1}$ , respectively 165 nm. For the Ti top-coatings a film thickness of 3 and 9 nm was applied.

### 2.3. Plasma polymer deposition

The plasma polymer coatings were performed within a capacitively coupled, radio frequency-driven (13.56 MHz) plasma reactor. A total fiber length of around 330 m was coated in each run by moving the fiber through the plasma zone at floating potential during the plasma treatment [21]. The deposition of the hydrocarbon (a-C:H) coatings was performed at 10 Pa pressure, 120 W power input and a gas flow rate of 30 sccm  $\text{C}_2\text{H}_4$  (Carbagas, Switzerland) with 99.95% purity. Oxygen-containing a-C:H:O coatings were deposited at the same pressure and power input with a gas flow ratio of 4:1 of  $\text{CO}_2$  (Carbagas, Switzerland),

purity of 99.998%, and  $\text{C}_2\text{H}_4$ . To sustain the same total gas flow rate, 24 sccm  $\text{CO}_2$  and 6 sccm  $\text{C}_2\text{H}_4$  was used for the a-C:H:O coatings. A 100 nm thick reference coating was performed with the a-C:H and the a-C:H:O deposition conditions on a silicon wafer and subsequently measured by contact profilometer (Dektak Bruker, USA). Thinner coatings as applied on the fibers with a nominal thickness as observed for the reference coating were performed with the same plasma conditions by adjusting the deposition time accordingly. For instance, a nominally 25 nm thick a-C:H or a-C:H:O film was deposited within 3 min or 5 min, respectively (on 330 m fiber each). Note that only directly exposed filament surfaces collect the maximum film thickness, while shadowed areas obtain less deposition.

### 2.4. Resistance measurement

The sheet resistances of the coated fibers were measured along the fiber via two gold coated copper contacts type LK4-B/SIL (Stäubli Electrical Connectors, Switzerland) with 4 mm diameter and a spacing of 1 cm connected to the measurement unit Keithley 2100 (Keithley Instruments, USA). The fibers were loaded with 50 g weight on each side when guided over the two gold contacts. At least 20 measurements were taken from each sample over a fiber length of 1.5 m.

### 2.5. Analyses of the morphology

The surface morphology of the coated fibers were studied by scanning electron microscope (SEM) Amray 3200-C at 2 kV acceleration voltage and electron current of 10  $\mu\text{A}$ .

### 2.6. Silver release

Silver release measurements were performed on silver coated fibers with a-C:H or a-C:H:O top coatings. Three samples of 4 m length were taken from each coated fiber and put in polystyrene test tubes. 4 ml ultrapure water ( $> 18 \text{ M}\Omega \text{ cm}$  according to ISO 3696) from a Milli-Q plus System (Millipore, USA) was added and stored between 6 h and 7 days at room temperature. After immersion in Milli-Q water, solutions were recovered, diluted in 2% nitric acid and then analyzed by ICP-OES using an Optima 3000 (Perkin Elmer) instrument (Ag lines 328.068 and 338.289 nm).

## 3. Results and discussion

The area of a fibrous structure is calculated according to Eq. (1). For the used fiber PET 150f48 with a fineness of  $15 \text{ mg m}^{-1}$  the total fiber surface was  $26 \text{ cm}^2 \text{ m}^{-1}$ . The comparative fiber PET 167f134 with  $16.7 \text{ mg m}^{-1}$  and 134 filaments (almost same weight per meter but 2.8 times more filaments) had a surface area of  $45 \text{ cm}^2 \text{ m}^{-1}$ . Fig. 1 shows a comparison of the electrical properties for the two considered PET fibers depending on the deposited Ag mass confirming that a higher surface area yields higher resistances for the same mass of silver applied. Fibrous structures are able to provide a high surface area. A larger amount of available surface area results in the distribution of the deposited silver over the surface yielding thinner coatings for the same applied Ag mass per fiber length. For thinner coatings film defects and non-uniformities between inner and outer filaments (Fig. 2) become more pronounced leading to higher resistance values.

The fibrous structure of the PET fiber 150f48 is shown in Fig. 2A which was further used throughout this study. Within the examined range of applied silver content of 1.7 and  $4.5 \text{ mg m}^{-1}$  (average film thickness of 62 and 165 nm, respectively) a similar (closed) film morphology was observed as can be seen in Fig. 2C and D. The granular surface indicates the typical columnar grain growth of the sputter-coated metal. Note that while the coating thickness is uniform along the fiber, a distribution in thickness was obtained over the cross-section with inner lying filaments collecting less coating.

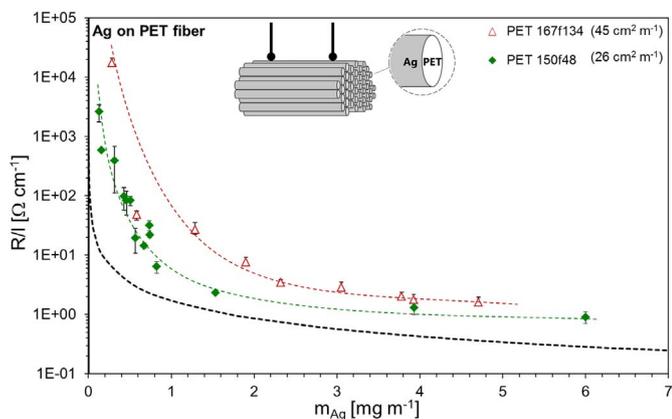


Fig. 1. Resistance in  $\Omega \text{ cm}^{-1}$  for a fiber with  $45 \text{ cm}^2 \text{ m}^{-1}$  ( $16.7 \text{ mg m}^{-1}$  and 134 filaments) and a fiber with  $26 \text{ cm}^2 \text{ m}^{-1}$  specific area ( $15 \text{ mg m}^{-1}$  and 48 filaments) depending on the deposited silver mass. The black dotted line represents the physical limit for the electrical resistance of bulk silver.

Plasma polymer films were deposited on top of the Ag-coated fiber as a (functional) diffusion barrier. While a-C:H coatings showed a typical (permanent) water contact angle (WCA) of  $78 \pm 3^\circ$  (low wettability), a-C:H:O coatings were hydrophilic with an initial WCA of  $45 \pm 3^\circ$  that changed to  $52 \pm 3^\circ$  during aging. The chemical composition was also analyzed by x-ray photoelectron spectroscopy: 5 at% O were measured at the surface (95 at% C) of the a-C:H coatings which reduced to  $< 1$  at% after short Ar sputtering, whereas 24 at% O and 76 at% C was determined for the a-C:H:O comprising carboxyl/ester, carbonyl and hydroxyl/ether groups [22].

Fig. 3A shows the morphology of the fiber surface after adding the a-C:H plasma polymer film with a nominal thickness of 25 nm acting as barrier layer on the PET fibers coated by  $1.7 \text{ mg m}^{-1}$  Ag. The plasma polymer-coated surface appears smoother, while the granular structure of the underlying silver layer is still visible yet less pronounced. For comparison the morphology of the titanium top coating is presented in Fig. 3B. The morphology was altered by Ti sputtering forming bigger

flat grains due to interdiffusion of Ti on the Ag surface. The sputter-deposition of the Ti layer was performed in metallic mode under vacuum [20]. Contact with oxygen after Ti deposition caused immediate oxidation (passivation) of the topmost layer (first nanometers) [16,23]. The morphology of the plasma polymer and the Ti coating after immersion in water (over 5 days) is shown in Fig. 3C and D, respectively. Water immersion does not yield swelling of PET fibers for the used conditions and the morphology was found to be largely unchanged without additional crack formation by expansion (or  $\text{Ag}^+$  diffusion). In the case of the Ti coating, surface charging under the electron beam during SEM measurement tended to be increased, indicating an advanced oxidation of the Ti top-coating during immersion in water.

Oxide layers as well as plasma polymer films, with an electrical conductivity of  $< 10^{-2} (\Omega \text{ m})^{-1}$ , can act as insulators with increasing film thickness [24,25]. Therefore, the electrical resistance of the coating system on the fiber was measured over a length of 1 cm at different positions along the fiber. Thus, the measured resistances included the low sheet resistance of the metal layers (Ag/Ti) and twice the contact resistance through the plasma polymer coating. The influence of the plasma polymer coatings (a-C:H and a-C:H:O) was studied for a nominal film thickness up to 180 nm, whereas the resistance of titanium coatings was determined for an average coating thickness of 9 nm at maximum, as shown in Fig. 4. The electrical conductivity of all plasma polymer coatings remained unchanged up to a film thickness of  $\sim 50$  nm. An increase in the electrical resistance was observed for thicker a-C:H and a-C:H:O coatings, yet still fulfilling requirements, e.g., for textile electrodes used as sensors. Along with increasing electrical resistance, an increase in mean variation was noticed.

The silver release from the silver film was determined by ICP-OES. The silver coated PET fiber (4 m) was immersed in Milli-Q water up to one week. The accumulative silver release from as-deposited Ag films with  $4.5 \text{ mg m}^{-1}$  is indicated by the dotted, orange line in Fig. 5. Already  $16 \mu\text{g}$  silver per one meter of fiber (equivalent to  $\mu\text{g ml}^{-1}$  or ppm for the selected conditions) was released after 6 h indicating a strong initial burst release. Since this value nearly reached the saturation limit of the solution, no further release was detected and the observed deficiency over a longer period might thus be explained by precipitation of

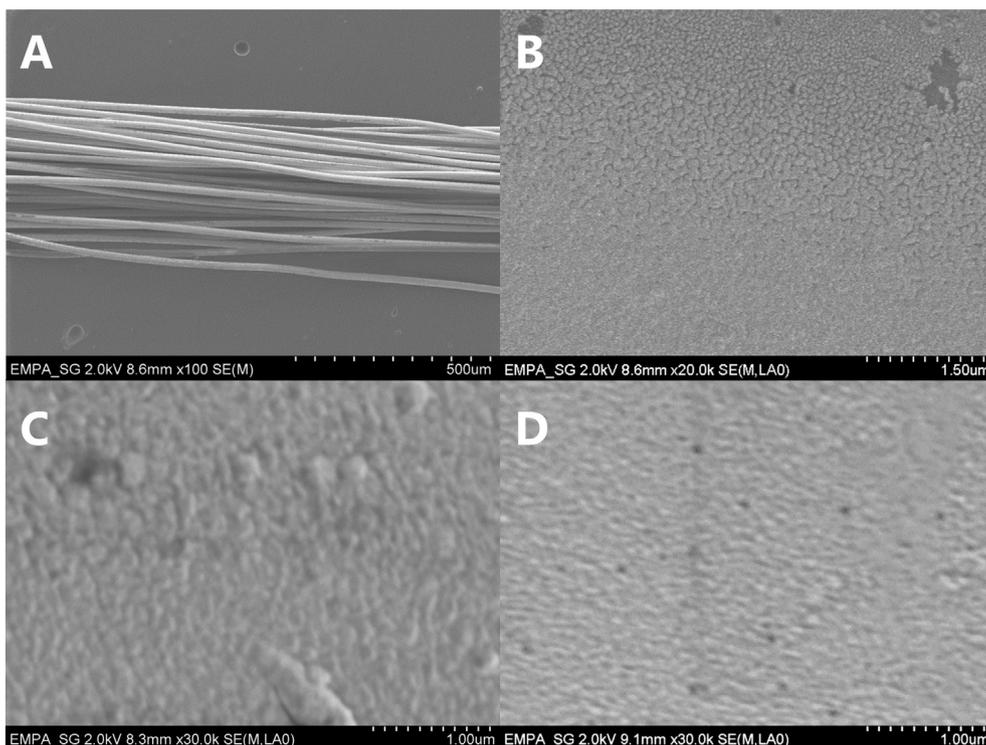
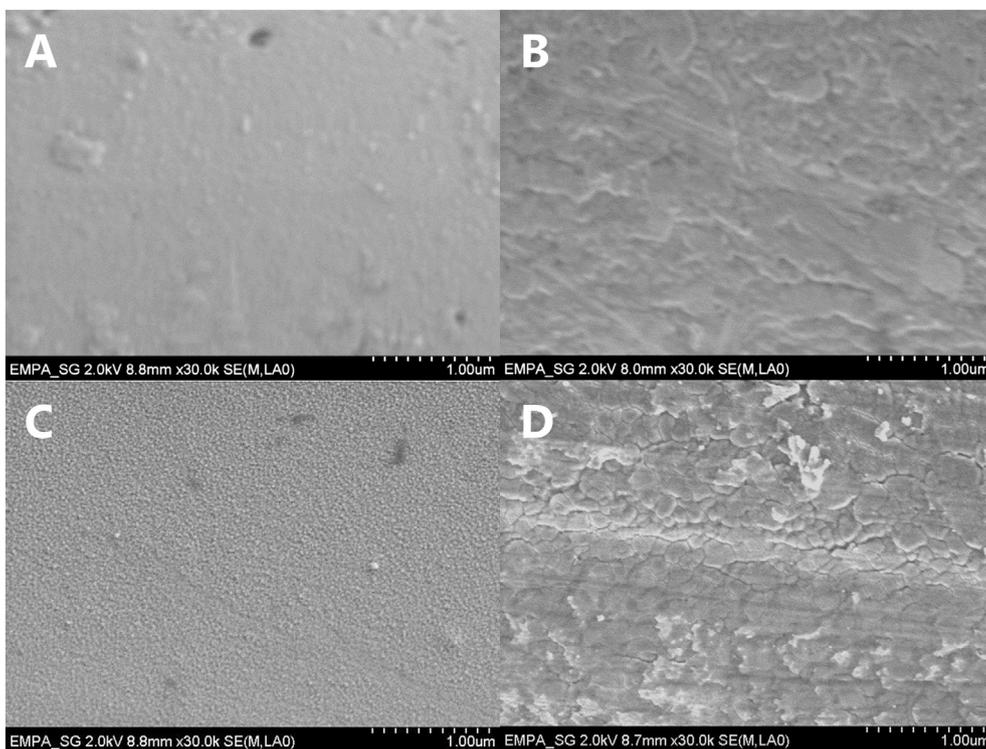
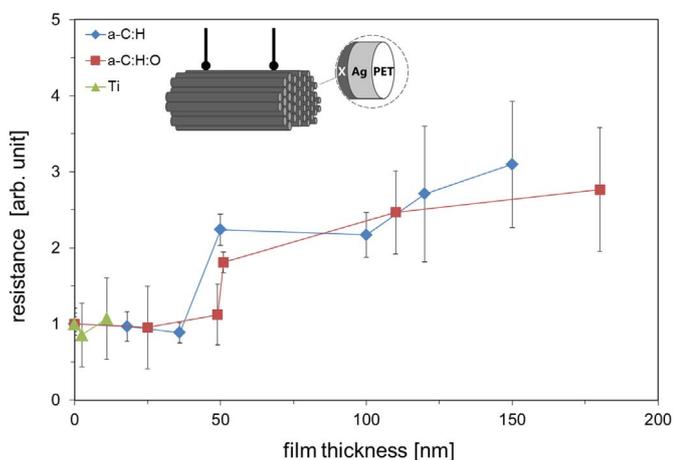


Fig. 2. Ag-coated PET 150f48 fiber (A) consisting of 48 filaments with a diameter of  $17 \mu\text{m}$  each. Decreasing film thickness around inner filaments can be recognized in (B). Outer filaments show a comparable Ag morphology for  $1.7 \text{ mg m}^{-1}$  (C) and  $4.5 \text{ mg m}^{-1}$  (D) silver coatings (62 and 165 nm average Ag thickness, respectively).



**Fig. 3.** SEM pictures of 25 nm a-C:H (A) and Ag/Ti surface with 9 nm Ti top coating (B) on PET 150f48. Same fiber surfaces shown after Ag silver release after 5 days in water: a-C:H (C) and Ti top coating (D).



**Fig. 4.** Electrical resistance (normalized to the initial value) of the silver coated fiber with a-C:H, a-C:H:O and Ti coatings. Mean variations are indicated by error bars.

silver. The black dashed line in Fig. 5 indicates the release from the PET fiber with lower silver content ( $1.7 \text{ mg m}^{-1}$  representing an average film thickness of 62 nm). The lower silver content (as deposited) showed a slightly reduced initial burst release, the steady state was reached later and precipitation was not observed within 7 days of immersion. The initial burst release mainly originates from a large surface area of naturally oxidized silver surfaces ( $\text{Ag}^+$  release from  $\text{Ag}_2\text{O}$ ) without requiring oxidative dissolution as limiting step [26]. These findings thus indicate that the coating with high Ag content covers a noticeably larger surface area on the PET fiber with predominantly very thin, oxidized layers or islands on the inner lying filaments (see Fig. 2B) which hardly contribute to electrical conductivity but strongly to Ag ion release.

All top coatings examined were found to delay the silver release. A 30 nm top coating of a-C:H (Fig. 5 left) on the PET fiber with high Ag amount was able to decrease the initial burst release, while still approaching the saturation level within the first days in water. The

nominally 150 nm thick coating, on the other hand, reduced the overall silver release by a factor of ten enabling moderate initial burst followed by steady release over several days. It can be inferred that parts of the Ag-coated (inner lying) filaments might not be reached by the plasma polymer film during deposition or only resulting in very thin coatings causing the observed high initial Ag release. On the contrary, the (thinner) a-C:H coatings on the fiber with lower silver content ( $1.7 \text{ } \mu\text{g m}^{-1}$ ) showed pronounced barrier properties against silver release. Already a 6 nm a-C:H coating reduced the release by a factor of 10, while a 25 nm a-C:H film caused a hundred time reduction. As discussed before, less distribution of Ag over the filaments at lower deposited mass enabled a more uniform coverage by the plasma polymer film effectively inhibiting Ag ion release.

Fig. 5 (right) presents Ag-coated fibers with functional a-C:H:O plasma polymer films compared to Ti-passivated silver coated fibers (with a Ag content of  $1.7 \text{ mg m}^{-1}$ ) [16]. The hydrophilic a-C:H:O coatings showed a low effectivity in reducing the overall silver release (independent of thickness), comparable to the 30 nm a-C:H coating. In addition to the already discussed distribution of the plasma polymer film on the single filaments, a-C:H:O enables water diffusion thanks to its polar groups. Thus mainly the initial burst release is reduced, while ongoing release (by oxidative dissolution) is promoted. Anyway, electrically conductive fibers can be functionalized, e.g. for adhesion improvement within composites or for cable coatings [21]. Finally, it should be noted that the observed smooth curves for Ag ion release indicate that the top-coatings remained intact during immersion in water acting as durable diffusion barriers, as also supported by SEM measurements (see Fig. 3C and D).

#### 4. Conclusions

The deposition of functional and barrier coatings on electrically conductive Ag-coated PET fibers carried out by plasma polymerization was investigated. Plasma polymer films of hydrophobic a-C:H and hydrophilic a-C:H:O maintained the electrical conductivity of silver-coated fibers over a broad range of film thickness still suitable for sensing applications. Plasma coating on PET fibers with large surface

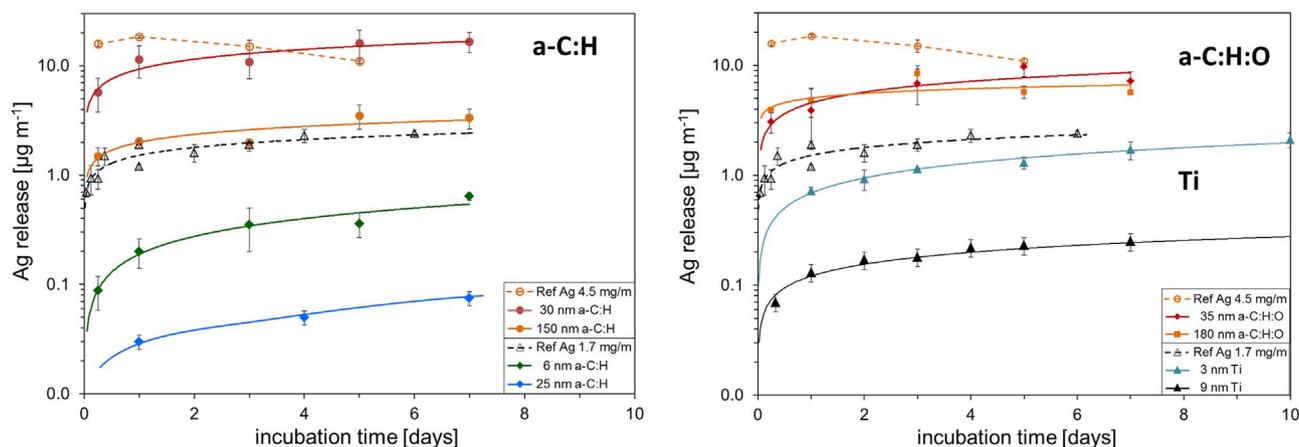


Fig. 5. Silver release kinetics of Ag-coated polyester fibers (150f48) as deposited with 4.5 and 1.7  $\text{mg m}^{-2}$  (dashed lines). Coatings were applied with different nominal film thicknesses for a-C:H (left) and a-C:H:O (right). For comparison also Ti top coatings (3 and 9 nm thick on average) taken from [16] are shown on the right diagram.

areas according to their multifilament structure, however, resulted in an uneven coating distribution, both for silver and plasma polymer films (with less coating on the inner lying filaments). Silver release kinetics were measured over 7 days immersion in water in order to examine the exposed (active) Ag surface area. The Ag ion release was found to be dependent on the amount of silver deposited on the fiber, acting as a reservoir, and on the thickness of the top coating. For fibers with a high silver amount ( $4.5 \text{ mg m}^{-2}$ ) a minimum (nominally) 150 nm thick a-C:H coating acting as a hydrophobic barrier layer had to be applied to also coat inner lying filaments and effectively reduce the Ag release below the potentially cytotoxic level ( $1 \text{ µg m}^{-2}$ ), since it is assumed that thin, oxidized Ag layers/islands cover the inner lying filaments largely contributing to the observed strong initial burst release. The Ag release from fibers with an overall lower silver content, on the other hand, was distinctly reduced already for ultra-thin a-C:H films with 6 and 25 nm thickness. Functional a-C:H:O plasma polymer films with up to 180 nm of nominal film thickness were also found to be stable on the Ag-coated fibers, but merely showed an attenuation of the initial silver burst release with high overall release rates due to its high water permeability. The difference in the observed silver release is thus related to the hydrophobicity (comprising a low or high amount of polar functional groups) of the two plasma polymer matrices, poor or rich in oxygen-containing groups. Anyway, a-C:H:O coatings are suited to enhance adhesion of metallized, conductive fibers for ultra-light cables or for embedding in composites. Hence, plasma polymer films on Ag-coated fibers are an alternative for recently studied  $\text{TiO}_x$  passivation layers as applied for ECG sensing depending on the requirements for different applications.

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