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Long-Term Stable Adhesion for Conducting Polymers in Biomedical Applications: IrOx and Nanostructured Platinum Solve the Chronic Challenge

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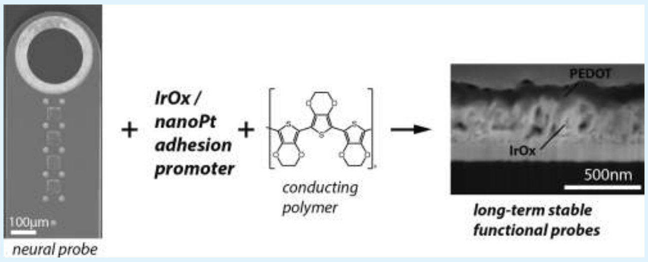

ABSTRACT: Conducting polymers (CPs) have frequently been described as outstanding coating materials for neural microelectrodes, providing significantly reduced impedance or higher charge injection compared to pure metals. Usability has until now, however, been limited by poor adhesion of polymers like poly(3,4-ethylenedioxythiophene) (PEDOT) to metallic substrates, ultimately precluding long-term applications. The aim of this study was to overcome this weakness of CPs by introducing two novel adhesion improvement strategies that can easily be integrated with standard microelectrode fabrication processes. Iridium Oxide (IrOx) demonstrated exceptional stability for PEDOT coatings, resulting in polymer survival over 10 000 redox cycles and 110 days under accelerated aging conditions at 60 °C. Nanostructured Pt was furthermore introduced as a purely mechanical adhesion promoter providing 10-fold adhesion improvement compared to smooth Pt substrates by simply altering the morphology of Pt. This layer can be realized in a very simple process that is compatible with any electrode design, turning nanostructured Pt into a universal adhesion layer for CP coatings. By the introduction of these adhesion-promoting strategies, the weakness of CP-based neural probes can ultimately be eliminated and true long-term stable use of PEDOT on neural probes will be possible in future electrode generations.

KEYWORDS: *conducting polymers, adhesion promotion, long-term stability, nanostructured platinum, electrodes, neural implant*

INTRODUCTION

The use of conducting polymers (CPs) as functional electrode coatings for neural microprobes has gained substantial interest in the past years, driven by the outstanding electrochemical properties of such materials in comparison to conventional metals.[1−4] The most relevant aspect is the possibility to fabricate microsized electrodes with low impedance and high charge injection capacity for bidirectional communication with neuronal tissue.[5,6] Further promising qualities, such as spatially confined release of drugs and biocompatibility, are key features making this class of materials very attractive for neural applications.[7,8] CPs, such as poly(3,4-ethylenedioxythiophene) (PEDOT), are typically electrodeposited into thin coatings on top of metallized probes. This relatively simple and cheap fabrication route offers the possibility for customized electrode functionalization and thereby complements the great potential CPs provide as electrode coatings.

Despite these attractive qualities, such CP coatings have not yet found their way into chronic biomedical applications. PEDOT that is electrochemically deposited in the presence of anionic dopants is frequently reported to be the most electrochemically stable conducting polymer available and it is expected to maintain its conductivity even over several years of implantation.[9−11] However, challenges in obtaining reliable adhesion between CPs and the noble-metal substrate ultimately stand in the way of exploiting the full capability of the material.[7,10,12−15] Noble metals like Pt, Pt−Ir, or Au, the most commonly used electrode substrates for neural probes, are not capable of forming stable covalent bonds to the polymer coating.[16,17] Adhesion is thereby mainly determined by physical interactions, such as mechanical interlocking, and is in consequence rather weak. If polymer coatings on noble metals are subjected to mechanical stress or exposed over a long time to a wet environment, as found in vivo, physical adhesion forces deteriorate quickly, which ultimately leads to delamination of the coating. This effect is additionally accelerated by the contraction/expansion of the polymer driven by the expulsion/incorporation of ions from the electrolyte that occurs under cyclic electrical load, as in cyclic voltammetry (CV).

The development of strategies for improving the adhesion of CPs on neural probes is therefore very important to bring the field forward and enable new generations of chronically usable

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implants. Reliable adhesion would furthermore be the key technology necessary for truly making use of the plethora of biofunctionalization opportunities CPs can offer.[18,19]

In response to the high interest in conducting polymer coatings for neural electrodes, different strategies to improve adhesion have recently been proposed in the literature. Green et al. showed that laser roughening of metal surfaces prior to polymer deposition resulted in improved adhesion for various conducting polymer−dopant systems.[13] Nevertheless, PEDOT/PSS coatings were still reported to delaminate upon steam sterilization or biphasic pulsing (864 M pulses at 70 μC/cm^2) from such treated surfaces while PEDOT/pTS and PEDOT/ClO$_4$ were found to be more stable. Laser-roughening technology is however restricted to large electrodes and thick metallizations, demanding different adhesion strategies that are compatible with neural microelectrodes. Cui and Martin reported on a "fuzzy gold" layer as adhesion promoter for polypyrrole (PPy) coatings.[15] It was shown that the polymer coating on such treated surfaces remained attached during measurements with 25 CV cycles while the coating from untreated substrates delaminated already after 5 CV scans. Usage of chemisorbed EDOT−acid as adhesion promoter between PEDOT and indium−tin oxide (ITO) was described by Wei et al.[20] Such treated samples survived up to 2 min of ultrasonication (with some delamination) while untreated samples delaminated already after 5 s under sonication.

Besides strategies that directly deal with adhesion improvement by means of a chemical or physical interaction on the substrate site, also various other strategies have been proposed to modify the polymer itself to yield a more stable coating. An example is the incorporation of carbon nanotubes,[21−23] which, however, mainly affects the cohesive polymer strength and has minor impact on the adhesion itself.

In the present work we address insufficient adhesion by investigating two novel adhesion-improving strategies with the aim of enabling true long-term stable use of PEDOT on neural probes. Nanostructured platinum (nano-Pt) as well as iridium oxide (IrOx) are introduced as adhesion promoters to provide a reliable and strong connection between noble-metal substrates and CP coatings. Both materials feature nanostructured topographies with high potential to mechanically anchor, thus stabilizing electrodeposited polymer coatings. Furthermore, we hypothesize that IrOx offers a chemical bonding to PEDOT, in addition to the physical binding forces, via carbide bonds, a mechanism that is not available for platinum.[16,17] In previous work we found that PEDOT on IrOx remained stable for more than 1000 CV stressing cycles, whereas PEDOT films on sputtered Pt delaminated already after 150 stressing cycles.[24] IrOx-stabilized PEDOT was furthermore found able to pass at least 600 M biphasic pulses (650 μC/cm^2) without any sign of delamination or degradation. This observation led to the assumption that IrOx not only provides a physical binding to the polymer but rather that also a chemical binding component must be responsible for the observed adhesion strength. By comparing nanostructured Pt and IrOx as adhesion promoter in this work, we will address this hypothesis and unravel the secrets behind the exceptionally strong binding mechanism. Nanostructured Pt thereby serves as control, providing similar morphology to IrOx but preventing the formation of stable carbide bonds to CPs.[17] At the same time, by introducing nanostructured Pt, we aim at providing a simple but very efficient alternative to IrOx as adhesion promoter. We test the adhesion promotion capability of both approaches by expanding the stress testing to extremes that have not been described in the literature before (10 000 CV cycles). Furthermore, we use an accelerated aging process to predict the long-term stability of PEDOT on smooth Pt, nanostructured Pt, and IrOx for the case when no stimulation is applied to the material, resembling the usage of the polymer on a probe for neural recordings. Activated IrOx (AIROF) is investigated in contrast to sputtered IrOx (SIROF) with respect to its quality as adhesion promoter, with identical IrOx chemistry for both substrates but providing different morphology and hence different physical adhesion forces. Besides PEDOT/PSS, also PEDOT/dexamethasone (PEDOT/Dex) is tested in combination with IrOx to evaluate the influence of the polymer dopant (here Dex) on the adhesion promotion in contrast to the contribution provided by the PEDOT backbone. Electrochemical, optical, and X-ray photoelectron spectroscopy (XPS) measurements are employed to evaluate the adhesion strength and to identify the binding mechanism for the proposed adhesion promoters.

■ MATERIALS AND METHODS

Sample Fabrication. Adhesion testing was performed using flexible polyimide electrodes of 10 μm thickness with sputtered platinum as the basic metallization layer, fabricated according to the process described by Stieglitz et al.[25] Samples with a bare Pt surface, and consequently without adhesion promoter, were directly used as fabricated. Nanostructured Pt was realized on a subgroup of the Pt samples using the deposition process described earlier by Boehler et al.[26] to provide a roughened Pt surface with similar morphology to IrOx but without the possibility of forming stable chemical bonds with CPs (Figure 1). For the sputtered IrOx adhesion promoter (further referred to as IrOx adhesion promoter in this text, in contrast to AIROF), a second sputter process was included in the cleanroom fabrication of the flexprobes subsequent to the Pt metallization. This sputter process was performed on a Leybold Univex 500 sputter device (Oerlikon Leybold Vacuum GmbH, Cologne, Germany) at 100 W with an O$_2$ flow of 15 mL/min, yielding an IrOx layer of 400 nm thickness. AIROF was realized by electrochemical oxidation of a pure Ir surface in phosphate-buffered saline (PBS, 0.01 M) using CV scans between −0.6 and 0.9 V vs Ag/AgCl.

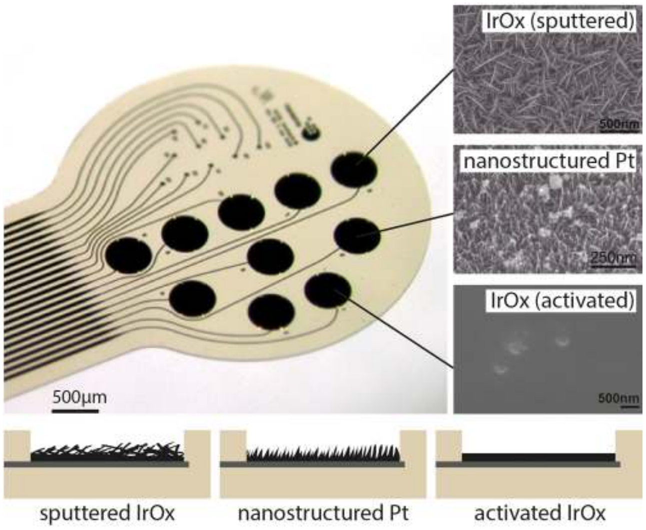

Figure 1. Thin-film polyimide electrode used for adhesion testing. SEM images on the right show the surface morphology of the adhesion promoters under evaluation. A sketch of the corresponding structure is provided at the bottom.

Before coating the samples with the conducting polymer, an electrochemical cleaning process was performed on all electrodes by means of CV in PBS (0.01 M) using a potential range of −0.6 to 0.9 V vs Ag/AgCl until a stable redox behavior was observed (typically 10 CV cycles). This process was used to ensure an electrochemically clean surface and therefore equal deposition conditions for the CP coating. Subsequent to the cleaning, PEDOT was potentiostatically polymerized on all probes at a potential of 0.9 V vs Ag/AgCl from an aqueous solution of 0.01 M EDOT and 5 mg/mL sodium polystyrenesulfonate (NaPSS) or 0.01 M dexamethasone 21-phosphate disodium salt (Dex). The polymerization was driven until a charge of 200 mC/cm^2 was reached on each electrode, corresponding to a coating thickness of approximately 1.3 μm.

EDOT (483028), NaPSS (243051), Dex (D1159), H_2PtCl_6 (206083), HCOOH (F0507), and PBS (P5368) were purchased from Sigma-Aldrich and directly used as delivered.

Adhesion Test Protocol. The adhesion of the PEDOT coating to the underlying substrate was assessed by applying electrochemical stress to the coating in terms of CV and observing the electrical as well as optical characteristics of the coating as measure for the adhesion quality. The stress in the polymer thereby results from incorporation and expulsion of ions from the electrolyte during CV scanning, which is associated with a respective swelling or shrinkage of the entire polymer. This effect can be used to apply mechanical force in a contact-free method to a thin coating that otherwise cannot be tested with conventional methods like shear or pull testing under wet conditions. The stress testing was performed on a Metrohm Autolab 302N potentiostat (Metrohm, Filderstadt, Germany) using repetitive stressing blocks of 20 CV scans (vertex potentials, −0.6 and 0.9 V; scan speed, 0.1 V/s) followed by an electrical impedance spectroscopy (EIS) measurement (10 mV_{Sin}, 10 kHz−0.1 Hz). PBS (0.01 M) was used as electrolyte and EIS was performed without external bias at open circuit potential (OCP). Such blocks were repeated until delamination of >20% of the coating could be optically verified under a microscope or a maximum count of 10 000 CV cycles was reached. For optical microscopy, the samples were rinsed with Milli-Q water and dried at room temperature prior to the imaging.

A second set of PEDOT-coated samples was exposed to accelerated aging conditions without further electrochemical stress being applied to the film. These samples were stored in PBS at 60 °C and in regular intervals taken out of the oven for EIS measurements as well as microscopy imaging. Quantification of the delaminated polymer areas from these probes was subsequently performed by image analysis using the program ImageJ. Microscope images were converted to black and white pictures so that the ratio of bright areas (corresponding to the delaminated parts) and dark areas (corresponding to the remaining polymer coverage) could be calculated and referred to the initially covered area of the electrode.

IrOx and Pt substrates were further immersed in aqueous solutions with either 0.01 M EDOT or 5 mg/mL NaPSS in order to evaluate whether the monomer or the anion react inherently with the substrate. These samples were stored at 60 °C for a time period of 400 h and regular EIS measurements were used to determine the electrochemical properties of the substrates, which in turn provides information about the binding of EDOT or NaPSS to the samples.

High-Magnification Imaging. Scanning electron microscopy (SEM) was performed on a Nova NanoSEM (FEI, Hillsboro, OR) with a nominal resolution of 1 nm. A cross-sectional imaging was recorded using a dual beam Strata 400 focused ion beam SEM (FIB-SEM) device from FEI at Karlsruhe Nano Micro Facility (KNMF, KIT, Karlsruhe, Germany).

X-ray Photoelectron Spectroscopy. XPS measurements were performed using a K-Alpha+ XPS spectrometer (Thermo Fisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[27] All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (30−400 μm spot size). The K-Alpha+ charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge buildup. The spectra were fitted with one or more Voigt profiles (binding energy uncertainty, ±0.2 eV). The analyzer transmission function, Scofield sensitivity factors,[28] and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2 M formalism.[29] All spectra were referenced to the C 1s peak of hydrocarbon at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au.

Sputter depth profiles were performed using a raster scanned Ar_{1000}^+ cluster ion beam at 8.0 keV, 30° angle of incidence, and a sputtered area of 1 × 2 mm^2.

■ RESULTS

PEDOT/PSS coatings were potentiostatically electropolymerized with a charge density of 200 mC/cm^2 on top of Pt, nanostructured Pt, and IrOx electrodes of 500 μm diameter, resulting in a homogeneous blue film on all substrates. Such polymer-coated samples were repetitively exposed to electrochemical stress by means of CV in order to challenge the polymer/substrate interface. Optical images as well as impedance measurements were taken after each 20th CV cycle to determine the polymer status. Results are summarized in Figure 2 for PEDOT on Pt as well as PEDOT on nanostructured Pt and IrOx. It can clearly be seen that the impedance of the polymer coating on both Pt-based substrates increased steadily with progressive stressing, while the impedance of the coating on the IrOx adhesion promoter remained essentially stable over the entire test period. It is important to note here that the impedance data is displayed for different CV counts for the three substrate materials. While PEDOT delaminated from Pt within 150 CV scans, the polymer on the nanostructured Pt remained attached for 1500 CV cycles and the coating on the IrOx survived even 10 000 CV scans, which was set as the end point of the test regardless of the polymer's status. From the insets in Figure 2 it can furthermore be seen that PEDOT on Pt delaminated in large pieces when the critical stress level was exceeded. In contrast to this, film failure from the nanostructured Pt was characterized by cracks and blister formation, finally leading to rather small delaminated polymer fragments. For PEDOT on IrOx, delamination could not be reached during the maximum applied number of 10 000 CV scans, and consequently, no detailed failure mechanism could be determined for this material combination. It is further worth mentioning that the initial impedance of all polymer-coated samples was similar (8.5, 9.2, and 9.5 kΩ for PEDOT/PSS on Pt, nanostructured Pt, and IrOx, respectively, determined below the cutoff frequency at 1 Hz), confirming a homogeneous coverage of the substrate with the polymer. In comparison to the impedance values of bare Pt (727 kΩ), nanostructured Pt (65 kΩ), and IrOx (24 kΩ), this constant impedance demonstrates that the electrical performance of the coated samples is defined by the polymer rather than the substrate. High-accuracy impedance fitting for all PEDOT/PSS-coated samples could further be obtained using the equivalent circuit model described by Bobacka et al.[30] Different blue shades of the PEDOT coating in the inset images in Figure 2 are determined by the microscope settings that were chosen for optimal image analysis and do not reflect different film thicknesses or oxidation states of the polymer.

In order to decouple the electrochemical actuation effect from the adhesion properties, a second set of samples was coated with PEDOT and exposed to accelerated aging conditions by storage in 60 °C PBS over a total time period of 2640 h (110 days). Results from this accelerated aging test,

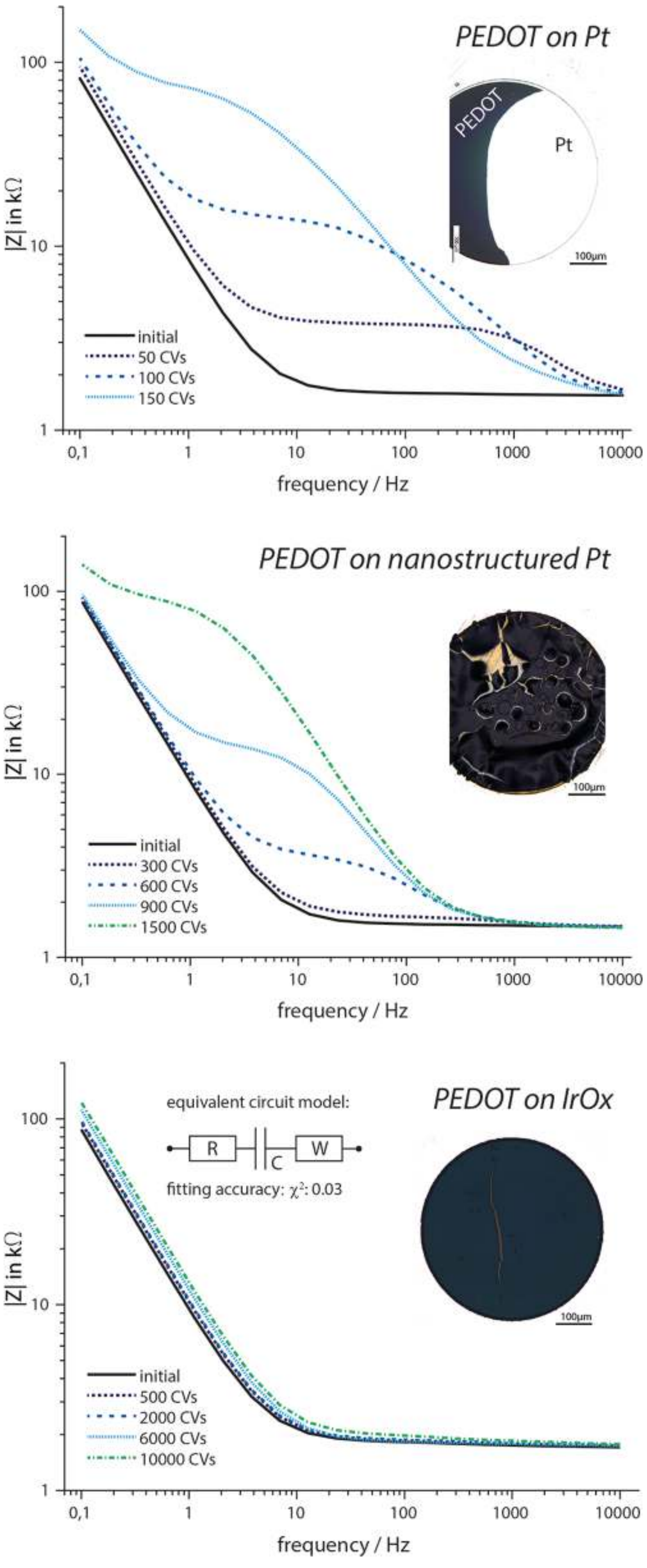

Figure 2. The dependence of electrical impedance measurements on the CV stressing for PEDOT/PSS on Pt (top), nanostructured Pt (middle), and sputtered IrOx (bottom). Insets show the polymer status at delamination for the Pt-based substrates and for IrOx at the end of the test period (after 10 000 CV cycles). Images and data are representatives of the five samples in each group. Impedance fitting using the equivalent circuit model described by Bobacka et al.[30] yields high accuracy ($\chi^2 = 0.03$) for PEDOT coatings on all substrates.

performed in the absence of any electrochemical stressing, are compiled in Figure 3. Also here a clear difference in the adhesion behavior of PEDOT toward the three substrate materials can be seen with progressing measurement time. The polymer delamination was found to be the most severe for the coating on top of Pt, where more than 50% of the PEDOT was lost within 600 h storage time. This was overall the highest degree of delamination observed during the entire test period for these samples. With nanostructured Pt as a mechanical adhesion promoter, delamination speed was significantly reduced and loss of 50% of the polymer coating was first reached after 2500 h storage time. The coating on top of IrOx did not show any delamination during the test period for all six tested samples. This is in good agreement with the impedance recorded during the first 1000 h of storage time, where PEDOT on IrOx showed a stable behavior (Figure 3b). In contrast, the impedance for PEDOT on Pt and nanostructured Pt clearly increased. Nanostructured Pt as adhesion layer by far outperformed the bare Pt. The failure mechanism, representative for all six tested Pt and nanostructured Pt samples, as observed during the test can be identified from Figure 3c. The leftmost picture shows the initial status with a homogeneous dark polymer coating. With progressing time, delamination of small fragments led to partial exposure of the underlying substrate, shown by the white areas in the images (II and III). The impedance changes corresponding to the three delamination images are highlighted in Figure 3b. Interestingly, the delamination mechanism in the accelerated aging study was found to be different from that of the previously shown delamination under cyclic voltammetry conditions.

To be able to distinguish between the morphological and the chemical contribution to the binding of PEDOT on sputtered IrOx, samples with pure Ir substrate were fabricated and subsequently oxidized into AIROF. The oxidation of Ir to IrOx, commonly referred to as activation, was done by CV in PBS and restricted to 25 CV scans with the intention of only modifing the surface chemistry without introducing substantial morphological changes. From the micrographs in Figure 1, it can be seen that the morphology of AIROF is flat, in contrast to that of sputtered IrOx or the nanostructured Pt. AIROF substrates were further coated with PEDOT and exposed to the same electrochemical stress protocol. The resulting impedance change (Figure 4) shows a progressive deterioration with increasing number of CV scans. Optical inspection of the coating revealed that the polymer did not delaminate; however, a significant change in color could be seen from initially dark blue to light blue/transparent after 1000 CV scans. Scratches, indicated by the arrow in the third inset picture in Figure 4, were intentionally added after the last measurement to distinguish between the remaining polymer and the metallic substrate and are not a result of the applied stressing. CV curves for PEDOT/PSS on AIROF are shown in Figure 5a, where a clear deterioration in conductivity is evident, along with the overall change in the CV shape, which is in accordance with the impedance alterations observed in Figure 4. For comparison, the CV curves of PEDOT/PSS on SIROF are provided in Figure 5b. For this material combination, only a minor change during the first few CV scans can be seen, which is associated with the initial reorganization of the polymer upon CV sweeping. The CV scans for PEDOT/PSS on SIROF remained stable after this point and the overall CV shape was preserved throughout the measurement, in contrast to the progressive changes for PEDOT/PSS on AIROF.

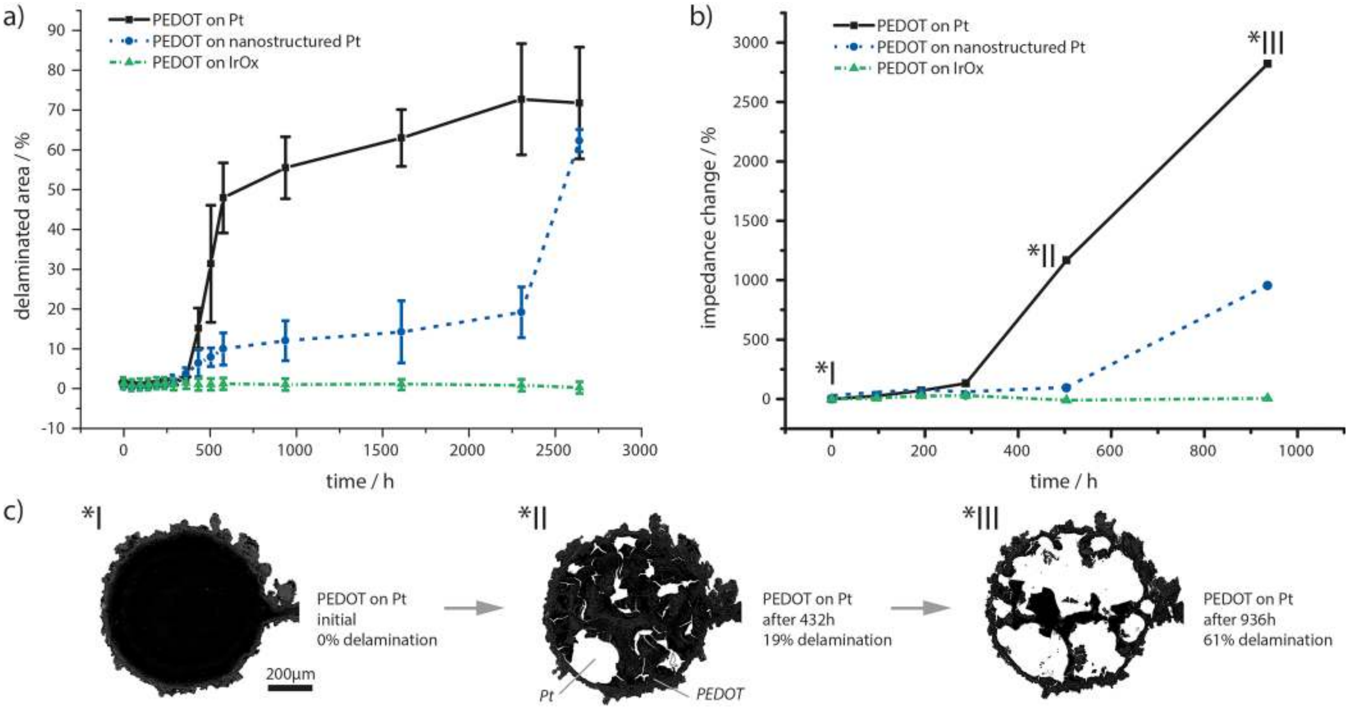

Figure 3. Accelerated aging results for PEDOT/PSS on Pt, nanostructured Pt, and IrOx showing the delaminated area over time (a) and the corresponding impedance changes (b). Representative microscope images at different times are displayed in panel c for PEDOT on Pt ($n = 3$ for Pt and nanostructured Pt, $n = 6$ for IrOx).

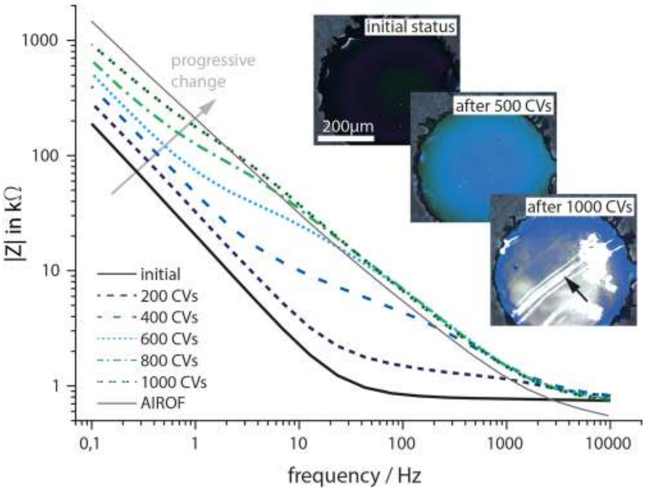

Figure 4. Electrical impedance data for PEDOT/PSS on activated IrOx surface under stress testing. From the inset pictures a progressive color change can be seen with increasing number of CV cycles, correlated to the changes in impedance. The scratches (highlighted by the arrow) were added subsequent to the measurements to distinguish between the metal substrate and the transparent polymer. Representative data from three samples.

In order to determine whether the adhesion of PEDOT to IrOx is dominated by the polymer backbone or the anion in the polymer system, different samples were fabricated using PSS or Dex as dopant and exposed to the CV-based stressing protocol. Both polymer systems demonstrated equal adhesion strength to the IrOx substrate over 1500 CV scans, as identified by constant electrochemical properties.

The chemical binding information between PEDOT and IrOx was investigated by XPS measurements of polymer-coated IrOx surfaces. Thereby an Ar_{1000+} cluster ion beam at 8.0 keV was used to sputter-ablate the polymer for creation of a depth profile with preservation of the chemical information. Note that Ar cluster ion beam sputtering cannot remove inorganic materials, and in consequence, the sputter depth profile will stop at the IrOx layer. With an XPS sampling depth of around 5−10 nm, the first measured Ir 4f signals when approaching the IrOx−PEDOT interface are therefore interface-related, whereas the Ir 4f peaks after removal of the organic layer represent the IrOx bulk state. The Ir 4f detail spectra was measured, fitted, and evaluated at the PEDOT−IrOx interface as well as for the IrOx bulk, as shown in Figure 6. After referencing all spectra to the C 1s peak of hydrocarbon at 285.0 eV, a small peak shift between the bulk and the interface state could be measured, as indicated by the dashed horizontal line in Figure 6. A corresponding C 1s component, as would be expected for an Ir−C bond, could not be verified with the applied techniques. XPS further proved identical IrOx stoichiometry for both the AIROF and SIROF films and in addition confirmed a smoother morphology for AIROF films in comparison to SIROF ones.

Aiming at further identifying possible binding partners, IrOx and Pt substrates were stored in aqueous solution containing either the EDOT monomer or the NaPSS counterion. Electrochemical measurements were used to verify whether the monomer or the PSS bind to the respective materials and thus influence the electrical impedance. Neither material showed any alteration of their electrochemical properties during 400 h of passive exposure at 60 °C.

The cross section of PEDOT−IrOx samples was further investigated by focused ion beam scanning electron microscopy (FIB-SEM) and compared to the cross section of PEDOT on nanostructured Pt. Despite the low contrast between metals and polymers in SEM pictures, a dense integration of the PEDOT into the porous structure of IrOx as well as into the

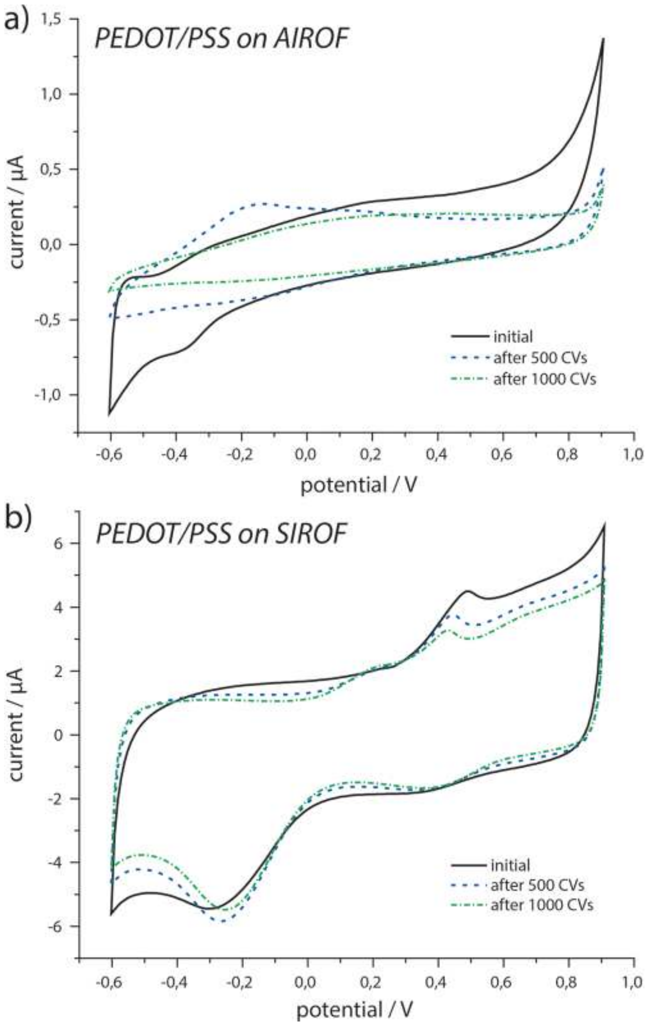

Figure 5. During CV cycling of PEDOT/PSS on AIROF (a), a progressive change in CV shape and overall conductivity can be seen. In comparison, PEDOT/PSS on SIROF (b) displays a stable CV signal. Measurements were performed in 0.01 M PBS between −0.6 and 0.9 V vs Ag/AgCl at a scan rate of 0.1 V/s.

pores of the nanostructured Pt could be identified, as shown in Figure 7. The inset figure displays nanostructured Pt without PEDOT, which allows a clearer view of the nanostructures when imaged without the polymer interference. Average roughness measured in terms of feature height for the two substrate materials was 177 ± 18 nm for IrOx and 130 ± 8 nm for nanostructured Pt.

■ DISCUSSION

Conducting polymers, and in particular electrochemically deposited CP systems based on PEDOT, have gained a lot of attention as a neural interface coating based on their excellent electrical properties in combination with their biocompatibility and ease of fabrication. The critical question on how to achieve and maintain long-term stable integration of such coatings with neural probes has however gained comparably little attention so far. Strategies for improving the adhesion of CPs are therefore currently insufficient. This has led to CP coatings often being associated with delamination and stability issues, which stand in the way of chronic biomedical applications.

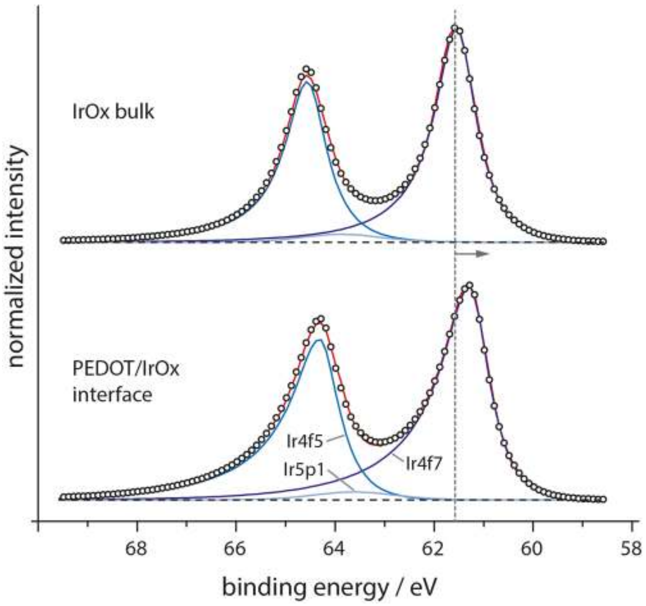

Figure 6. Ir 4f XPS detail spectra, measured for bulk IrOx (top) and at the interface between PEDOT and IrOx (bottom). A small peak shift around 61.3 eV is highlighted with a vertical dashed line. For better visualization, the peaks are normalized to maximum intensity.

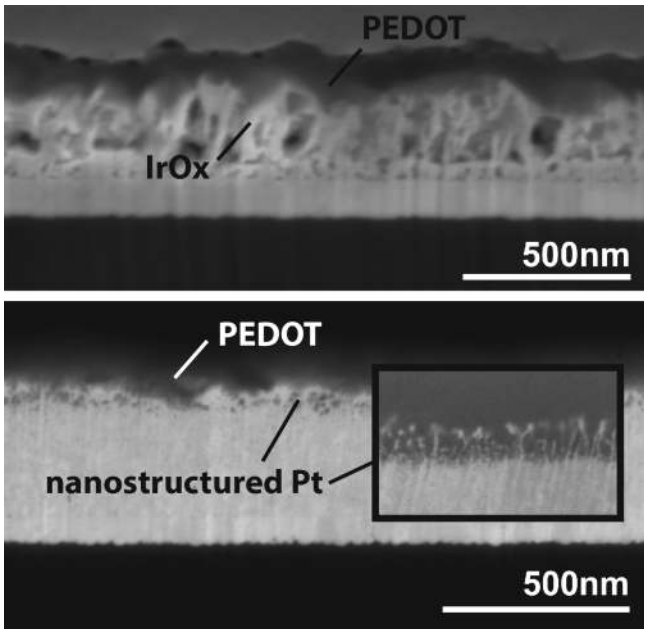

Figure 7. FIB-SEM image of the interface between PEDOT/PSS and IrOx (top), compared to that of PEDOT/PSS and nanostructured Pt (bottom). A dense integration between the metal (bright structures) and the polymer (dark shades) can be identified in both cases. The inset in the lower image shows nanostructured Pt without PEDOT, which allows clearer imaging of the Pt structures.

In our work we have successfully addressed this weakness with two novel strategies that can easily be integrated with standard microfabrication processes and that lead to extents of stability that have not previously been reported in the literature. Sputtered IrOx showed by far the best adhesion promotion for the PEDOT film, while nanostructured platinum was only slightly inferior in supporting the polymer coating. The CP film on IrOx survived the extreme stressing conditions of 10 000 CV scans as well as accelerated aging in 60 °C PBS for more than 110 days without delamination. This is to our knowledge the longest test period applied to conducting polymers and, consequently, the longest timespan where stable adhesion of a PEDOT coating has been demonstrated. In fact, the vast majority of studies rarely exceed 25 CV cycles (e.g., 5 cycles in ref 31, 10 cycles in ref 13, or 25 cycles in ref 15), and the highest CV numbers reported are 400 cycles in ref 9, 1000 cycles in ref 32, 3000 cycles in ref 22, and 6000 cycles in ref 33.

Our investigations furthermore showed that nanostructured Pt featured superior adhesion to the polymer coating in comparison to smooth Pt. Since both metal layers have the same chemical composition, it is thereby only the topography that enabled the significant adhesion improvement. This finding is particularly interesting considering the simple fabrication process of the nanostructures which can essentially be applied to any electrode type subsequent to the general probe fabrication. By such means, an efficient way to support CP coatings on neural probes can be accomplished where the polymer film exhibits an adhesion strength at least 1 order of magnitude higher compared to the smooth surface and was found sufficient for up to 1500 CV cycles.

By comparing the stability of PEDOT on nanostructured Pt and IrOx, a 7 times higher adhesion strength could be determined for the polymer on the IrOx surface. Since both adhesion promoters provide similar roughness (177 ± 18 nm for IrOx vs 130 ± 8 nm for nanostructured Pt), this suggests that the adhesion between PEDOT and IrOx must be determined by a combined mechanical and chemical bonding. In our XPS studies we were however not able to find clear evidence for such a chemical binding with the applied techniques. It is thereby worth mentioning that a possible binding could also not be excluded by the obtained data. As a consequence of the rough morphology of IrOx, the chemical information recorded in XPS depth profiling included both bulk and interface states from PEDOT and IrOx, so that only averaged chemical information could be measured. From this data we could see a small peak shift when comparing the Ir 4f peak recorded from the PEDOT−IrOx interface region with the signal from the IrOx bulk regions determined after removal of the PEDOT coating. However, this weak chemical shift cannot clearly justify Ir−C binding, since the corresponding C1s component could not clearly be identified from the measured data.

One might argue that the strong adhesion could result from bond formation with the polyanionic dopant (PSS), which would stabilize the polymer/dopant complex. In order to investigate this, samples were prepared where PSS was exchanged for Dex as counterion in the deposition process. Since PEDOT/PSS and PEDOT/Dex coatings were found to adhere equally well to the IrOx substrate, we expect that the binding strength is thereby mainly determined via the PEDOT site and that the counterions (here PSS or Dex) play a minor role in this process. Contrary to the adhesion, it is nevertheless known that the cohesive strength of a CP film can be significantly influenced by the counterion, which hence plays an important role for the overall stability of the polymer.[10] Exposing Pt and IrOx substrates to an aqueous solution with either EDOT or NaPSS did not alter the electrochemical properties of the substrates during 400 h of exposure. From this we conclude that the monomer does not inherently bind to the IrOx surface. Instead, the bond seems rather to be formed during the electropolymerization reaction itself.

Idla et al. reported previously on the finding that PPy adheres exceptionally well to chemically oxidized titanium, maintaining stable adhesion during 6000 reduction/oxidation cycles (−0.9 to 0.2 V vs Ag/AgCl, 220 mV/s).[33] While they concluded that the enhanced adhesion is mainly based on the incorporation of Ti_xO_y into the PPy during film deposition, also a chemical binding was considered possible between oxidized Ti and PPy.[34] Despite that no binding mechanism was identified in the paper, their finding speaks for a similar effect between metal oxides and conducting polymers and supports our hypothesis of a chemical bond.

In order to discriminate between mechanical and chemical effects, a comparably smooth IrOx version could be provided in the form of AIROF with topographical features below a few nanometers, in contrast to sputtered IrOx. The surface chemistry of both materials was thereby identical, as proven by XPS measurements. If mechanical effects dominate adhesion to IrOx, PEDOT on the smooth AIROF should behave similarly to PEDOT on smooth Pt. In contrast, we found that PEDOT did not delaminate from the AIROF over at least the 1000 CV cycles tested. Interestingly, we could instead observe what appeared to be electrochemical deterioration of the polymer structure, as evidenced by loss of conductivity in correlation with a colorimetric change from blue to a light blue, transparent material, both typical signs of over-oxidation.[35] From the data in Figure 4, it is evident that the film on AIROF did not delaminate, since delamination would bring the original surface back and thereby also the original impedance. What can be seen is rather an insulating film adhering to the electrode, making the impedance after 1000 sweeps worse than the original state. The transparent coating can furthermore be distinguished optically from the Pt surface under a microscope, verifying the existence of a semitransparent film. It should be noted that, with decreasing electroactivity, the mechanical stress will also be decreased when the film no longer actuates to the same extent. It could therefore not be excluded that over-oxidation in this way offers a certain protection for the coating against actuation-driven delamination. However, over the first 500 CV scans, the transferred charge was only found to be reduced by 26% (after 1000 CV cycles by 46%), which speaks for the stress experienced still being comparable with that of samples on other surfaces.

PEDOT would be expected to be electrochemically over-oxidized at potentials exceeding 1.1 V vs Ag/AgCl.[35] Since the IrOx-stabilized samples could survive at least 10 000 cycles up to 0.9 V, without any sign of deterioration, a similar effect would have been expected also on AIROF. The over-oxidized film shown in Figure 4, however, indicates that the AIROF surface itself interacts with the deposited PEDOT, making it more vulnerable to oxidative attack. To the best of our knowledge, this effect has not been reported previously in the literature. Since the focus of this paper was adhesion promotion, it was beyond the scope to identify the responsible mechanisms for this unexpected effect. Nevertheless, the CV sweeps shown in Figure 5 clearly demonstrate a progressive electrochemical alteration for PEDOT/PSS on AIROF, while the same polymer film on SIROF remained electrochemically stable. The literature suggests that IrOx itself can act as an oxidant and, for example, nanoparticles of IrO_2 have been used to drive oxidative formation of PEDOT on their surface.[36] This would support the idea that the interface can accelerate oxidation, thereby weakening the polymer system. Why this would occur on the AIROF surface and not on the sputtered IrOx is, however, unclear and should be addressed in future work. Thereby also the question whether electrodeposited IrOx would be suitable for adhesion promotion should be investigated by considering applications where the adhesion promotion of nanostructured Pt might not be sufficient and SIROF cannot be used.

In a study by Cui and Martin,[15] a "fuzzy gold" layer of similar morphology to the sputtered IrOx in our study was investigated as a supporting layer for conducting polymers. They showed that PPy survived 25 CV scans on top of such structured surfaces before delamination began for thick polymer coatings. Unsupported polymer films showed initial delamination after only 5 CV scans in their study. Consequently, the roughened gold surface could promote a 5 times higher adhesion strength, which would accordingly also be expected for IrOx based on the similar morphology to the fuzzy gold. IrOx, however, showed a more than 67 times higher adhesion to the polymer in our study (meaning stable adhesion beyond 10 000 CV cycles). This further supports that the adhesion cannot solely be based on the mechanical interaction with the rough metal but must be significantly supported by a chemical contribution.

For PEDOT coatings on nanostructured Pt we found a 10-fold increased adhesion strength compared to that of smooth Pt, which is in a similar range as that observed for the rough gold layer by Cui and Martin. It is, however, worth mentioning that PEDOT on nanostructured Pt survived a total amount of 1500 CV cycles, in contrast to the 25 CV cycles reported for the fuzzy gold. It can thus be concluded that the morphology of the roughened substrate plays a significant role for the adhesion promotion. Since nanostructured Pt appears to provide smaller feature dimensions than the fuzzy gold, we hypothesize that smaller structures provide an overall higher adhesion strength than larger morphologies. Further studies with various different size ranges should however be invested in the future to verify this assumption.

In this study, we used cyclic voltammetry scans to apply stress to the polymer coatings. This type of signal might not seem ideal to provide realistic stress conditions to the polymer, since stimulation of neural tissue is typically done by fast biphasic current pulses. Nevertheless, it is a well-known fact that CPs experience some shrinkage or expansion as a consequence of the release or uptake of ions from the supporting electrolyte into the polymer bulk during CV sweeping. This effect involves a mechanical deformation of the polymer, which ultimately leads to forces acting at the polymer/substrate interface. In consequence, CV scans offer a simple yet efficient method to challenge the adhesion of soft and thin CP films on a substrate and therefore were chosen to accelerate delamination in this study. It should be noted that stress levels reached by this method do not reflect typical conditions seen in clinical usage of CPs under stimulation but serve as an accelerated adhesion test protocol. Biphasic current pulsing, employed in neural stimulation, is not expected to involve such high stress levels, and adhesion testing with this type of signal was furthermore covered in previous work by Boehler et al.[24] Additionally, it has recently been shown that CV cycling can be used as an efficient way to drive drugs out of drug-loaded CP films, turning CV cycling into a possible application scenario for biofunctionalized CP coatings.[37]

Besides the active stress testing, also a passive test employing accelerated aging conditions was performed to exclude any direct effect of the applied CV scans on the polymer adhesion. We thereby used a temperature of 60 °C for acceleration of delamination processes. This temperature has previously been reported to be suitable for accelerated aging tests of polymers, while higher temperatures were reported to cause a breakdown within the polymer and were thus not recommended for accelerated aging experiments.[38−40] According to Arrhenius law, storage at 60 °C provides an acceleration factor of 4.92 in comparison to body temperature (37 °C) or 11.31 if compared to storage at room temperature (25 °C). Taking these factors into account, our accelerated aging predicts a time of at least 1.5 years (tentatively much longer) of stable adhesion of PEDOT on IrOx at body temperature, which extends far into chronic conditions as defined in the field of medical devices. The corresponding lifetime on nanostructured Pt could similarly be estimated to be 1.3 years. A similar aging study has been performed by Venkatraman et al., where PEDOT/PSS coatings on top of PtIr wires were exposed to physiological solution at 67 °C for 28 days.[32] After this time frame, corresponding to 0.6 years at 37 °C, significant degradation of the coating was, however, reported. This measurement demonstrates that Ir in the form of an alloy is not capable of forming a stable bond to CPs and only pure IrOx seems to serve as a suitable adhesion promoter for CPs.

CONCLUSION

We here demonstrate that nanostructured Pt and sputtered IrOx both serve as outstanding adhesion promoters for CP coatings. Both materials are biocompatible, simple to apply, and compatible with conventional micromachining techniques. Adhesion over 10 000 redox cycles demonstrates exceptional polymer stability under stimulation conditions and suggests even longer survival of the coating if the film is only used for recording applications. We therefore believe that both strategies will be extremely useful for any application where long-term stability of CPs is demanded, including neural interfaces, sensor applications, or drug/molecule delivery systems.

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Notes

The authors declare no competing financial interest.

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