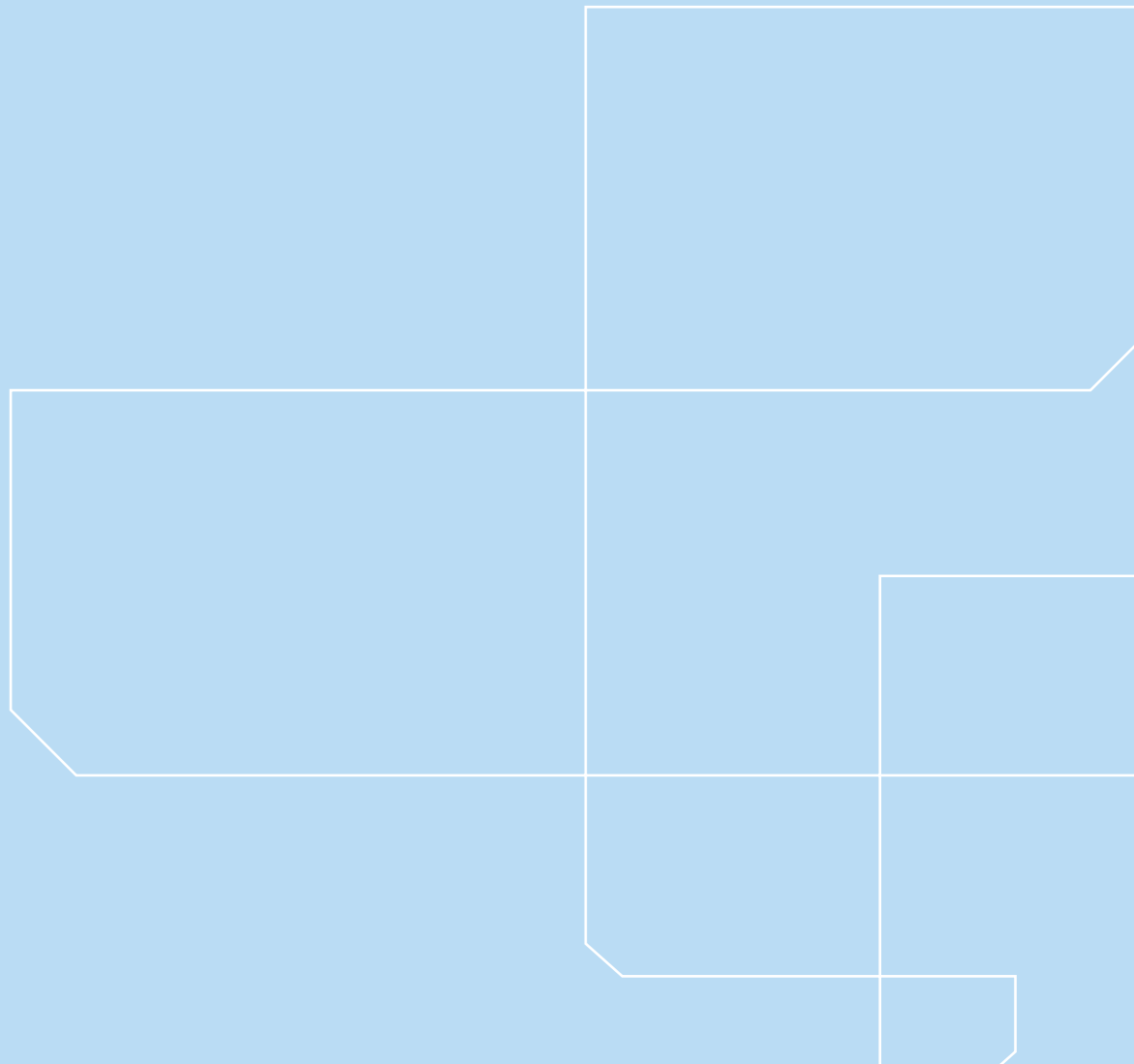


# LOW IMPEDANCE COATINGS FOR ENHANCING STIMULATION AND SENSING PERFORMANCE OF ELECTRODES

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# 1. INTRODUCTION

The range of electrode materials for state-of-the-art finished medical devices for sensing and stimulation application is limited. Current commercial devices mainly use uncoated metal electrodes made of Pt, Pt90Ir10, also referred to as PtIr, or Au. The need for biocompatibility and high electrochemical performance, along with the restrictions from manufacturing processes, imposes many limitations on the types of materials that can be used for these applications. Advanced materials with low impedance and high charge storage capacity are desired. These materials should increase the signal-to-noise level and enable improved signal quality in high-definition sensing. They should also be able to support the miniaturization of devices with increased electrode density, enabling high spatial resolution and therapy specificity.<sup>1</sup>

Advanced electrodes for pacemakers are typically made of coated PtIr base material. Due to inherent electrochemical limitations of bare PtIr, such as high impedance and low charge storage capacity, these electrodes are usually coated with TiN, Ir, or IrOx, which are highly porous and enable significantly faster charging/discharging processes due to reduced impedance, low polarization (TiN),<sup>2</sup> and availability of additional redox sites (IrOx).<sup>3</sup> In pacemakers, these coatings increase the sensing efficiency of the closed-loop stimulation (CLS) sensor, enabling proper physiological heart rate adaptation. In contrast to pacemakers, most of the currently available commercial devices for electrophysiology and neurostimulation still use uncoated metal electrodes consisting of Au, Pt, or PtIr. However, with advances in the medical device industry and its technologies, this may change in the future as closed-loop stimulation is adapted to neuromodulation devices as well. The new market will increase the demand for electrode materials, which can provide better electrochemical performance and higher-resolution sensing than uncoated electrodes.

With several limitations of traditional coating technology, certain device manufacturing steps are not compatible with either the coating or coating process. For example, centerless grinding used during a neuro-lead manufacturing process to yield the concentricity of the device will tear off the coating from the electrode surface, thereby challenging the application of coatings at the component level. Similarly, it is not cost-efficient to use a coating method like PVD for an assembled device, as it will require complex and selective masking of the device.

In addition, the high temperatures often generated during the sputter process are not always compatible with the polymeric insulation material. In these cases, alternative coating solutions like, Ampliccoat<sup>®</sup> or inkjet printed Pt and IrOx coatings are better options.<sup>4</sup> These coatings can be selectively coated onto finished devices' electrodes and do not require any masking. Hence, it is not only the high performance of the materials but a combination with a suitable manufacturing process that determines the application of these coatings on EP and neuro devices.

Unfortunately, getting an overview on the performance of all available materials is not an easy task. While a lot of independent work has been published on such electrodes and coatings, a consistent comparison cannot be found in literature, since electrode geometries and testing conditions differ widely within these reports.<sup>5, 6, 7</sup> On a qualitative basis, the potential of different materials is understood very well, but it is extremely difficult to find a consistent comparison of different materials in a quantitative way. This makes it highly challenging to choose the best electrode material for a given application.

To solve this issue, we have conducted a thorough study comparing bare PtIr electrodes with laser textured PtIr electrodes and different coatings, such as TiN, IrOx and PEDOT based Ampliccoat<sup>®</sup>. These electrodes and the coating types differ in their electrical performance as well as in their deposition methods. With this publication, we aim to provide a toolkit of available electrode materials and support the selection of the appropriate material for the desired stimulation, sensing or recording application.

## 2. MATERIALS AND METHODS

### 2.1 MATERIALS

#### Substrates

Foils of PtIr (Heraeus Deutschland GmbH & Co. KG) with a dimension of 25 mm x 6 mm x 100  $\mu\text{m}$  (B x W x H) were used as base electrode material.

#### Electrode Size

To ensure that the same electrode surface area is used for all electrochemical characterization, the PtIr substrate (coated or uncoated) was masked with a polymer tape, so that only a circular opening with an area of 1 mm<sup>2</sup> was left exposed for the characterization.

## Laser Structured Electrodes

For the laser structured electrodes, the PtIr foil was structured with a femtosecond laser.

## Coated Electrodes

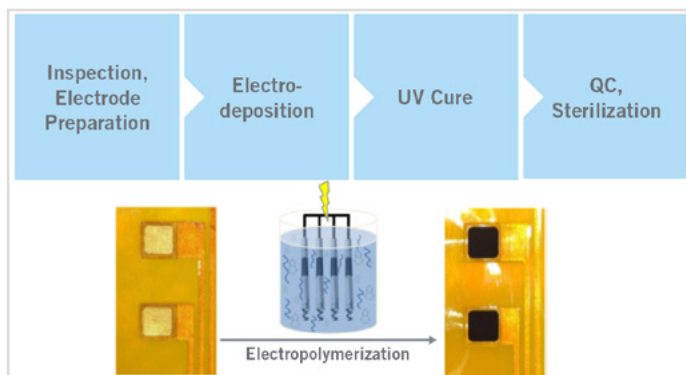
PVD coatings (IrOx, TiN) were applied onto the PtIr electrodes in standard coating thickness ranges, namely 4  $\mu\text{m}$  of TiN and 0.4  $\mu\text{m}$  of IrOx. The second type of coating is the proprietary biocompatible PEDOT based conductive polymer coating Amplicoat<sup>®</sup>, which has been developed and commercialized by Heraeus Medevio. Amplicoat<sup>®</sup> shows improved electrical performance as well as mechanical durability if compared to conventional PEDOT: PSS formulations.

## 2.2 COATING DEPOSITION METHODS

### Physical Vapor Deposition (PVD)

The DC Magnetron sputtering for TiN and IrOx has been described previously in detail.<sup>8</sup> These coatings can be deposited as single or multiple layers, and the electrodes can be coated in volume at the same time. Due to their inorganic nature, they exhibit excellent mechanical stability on metal electrodes.

### Electrochemical Deposition



**Figure 1.** Schematic representation of Amplicoat<sup>®</sup> deposition process.

Amplicoat<sup>®</sup> is formed via electrochemical deposition. This dark blue coating can be applied on final devices as well as on components without any masking requirements (**Figure 1**). The deposition process is largely independent of electrode shape and size and thus has several advantages compared to PVD coatings. It can be done either on a single device or in larger batches.

For this study, the coating was deposited onto the bare PtIr foils (Amplicoat<sup>®</sup>) and onto a laser-structured PtIr surface (Amplicoat+). Amplicoat+ is the name given to Amplicoat<sup>®</sup> deposited onto a laser-structured surface. The electrochemical performance of both Amplicoat<sup>®</sup> and Amplicoat+ are comparable, but Amplicoat+ has a significantly improved mechanical stability for chronic applications.

## 2.3 COATING CHARACTERIZATION METHODS

### Electrochemical Analysis (PEIS, CV)

Prior to characterization, all electrodes were cleaned with isopropanol to ensure a clean electrode surface. They were then electrochemically characterized with a Gamry Reference 600 Potentiostat in a 3-electrode setup with an SCE reference electrode and Pt counter electrode in PBS solution at room temperature. The PBS solution was degassed with N<sub>2</sub> prior to the measurement to ensure inert conditions and avoid any oxidation and reduction due to the presence of oxygen in PBS. Prior to any measurement, the open circuit potential was determined, and 50 sweeps from  $-650$  mV to  $+750$  mV vs. SCE were carried out at a scan rate of 300 mV/s to yield an activated surface and achieve a steady-state condition of the electrode surface. Cyclovoltammetry curves were then measured for a range of  $-650$  mV to  $+750$  mV vs. SCE at a scan rate of 100 mV/s to determine the charge storage capacity of the electrodes. Next, an electrochemical impedance spectroscopy was done with an excitation amplitude of 10 mV at open-circuit potential.

## Voltage Transient Measurements

Voltage transient (VT) measurements were done using a STG4008-16mA from multichannel systems. An oscilloscope (LeCroy Wavesurfer 434) was used to record the voltage response of the current pulses. For the tests, the electrodes were placed in a beaker with 1x PBS, and a Pt mesh was used as a counter electrode. A cathodic first biphasic current pulse with a pulse width of 200  $\mu\text{s}$  and an intra-pulse delay of 20  $\mu\text{s}$  was used. The maximum charge injection capacity (CIC) of each electrode type was determined according to the method suggested by (Cogan, 2008). Briefly, the applied current amplitude was increased in steps till the maximum cathodic polarization  $E_{\text{mc}}$  in VT curves reached the maximum cathodic safe limit of the electrode. This can be calculated by adding the open circuit potential (OCP) and the cathodic safe limit of the electrode determined by CV measurement in PBS. The CIC was then calculated using the following formula:

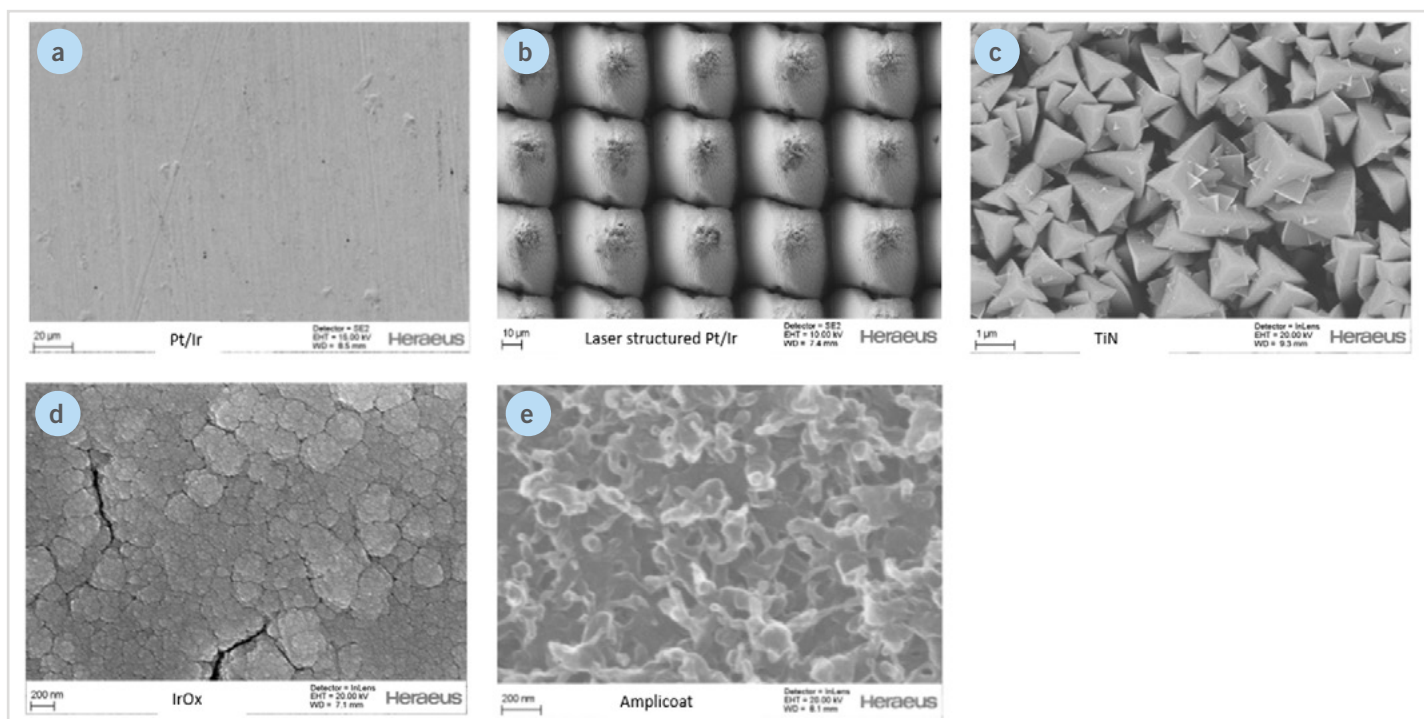
$$\text{CIC} = \frac{(\text{Maximum current (A)} \times \text{pulse width } (\mu\text{s}))}{(\text{Area of electrode (cm}^2\text{)})}$$

## Morphological Analysis

High-Resolution surface analysis was done using a Zeiss Ultra 55 scanning electron microscope at an acceleration voltage of 10-20 kV.

# 3. RESULTS & DISCUSSION

## 3.1 COATINGS AND THEIR MORPHOLOGY



**Figure 2.** SEM images of bare PtIr substrate (a), laser structured PtIr substrate (b), PtIr substrates coated with TiN (c), IrOx (d), and Amplicoat (e).

**Figure 2** shows SEM images of the investigated electrodes with their different topographies. As shown here, the untreated PtIr has a flat surface topography with some tool marks from the manufacturing process. **Figure 2b** shows PtIr after laser structuring, a favorable surface modification method for bare PtIr electrodes that increases its surface area without adding any new material to it. The laser structuring process does not require any masking and can be applied to a wide range of electrodes and devices, including components and finished devices. However, the laser patterning depends on the thickness of the substrate, and in cases of very thin electrodes, i.e., thickness in the sub-micrometer range, it can be challenging to pattern the surface. In these cases, the coating materials described below would be preferable.

Alternatively, the double-layer capacitance of a PtIr electrode can be increased by applying inorganic coatings like TiN and IrOx or a conductive polymer like PEDOT-based Ampliccoat<sup>®</sup>. **Figure 2c** shows the porous pyramidal morphology of TiN, as described in Thornton's zone model.<sup>9</sup> This is typical for TiN coating and causes its superior electrochemical performance.<sup>8</sup> IrOx-coated samples also depict an enlarged surface area with cauliflower-like morphology (**Figure 2d**), as reported previously by Cogan et al.<sup>10</sup> The SEM image of Ampliccoat<sup>®</sup> (**Figure 2e**) also shows a porous and rough surface with an increased total electroactive surface area which improves its electrical properties.

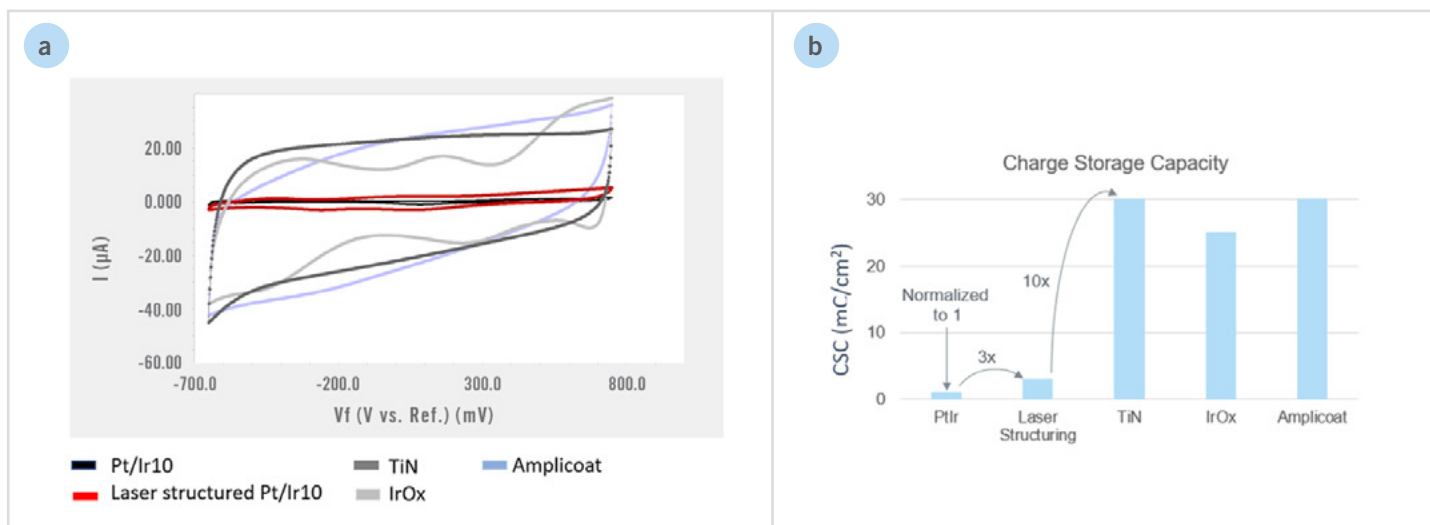
### 3.2 ELECTROCHEMICAL PERFORMANCE

#### Cyclo-Voltammetry

In **Figure 3**, exemplary cyclovoltammetry (CV) curves are shown for each of the different electrode types with a sweep range of  $-650$  mV to  $+750$  mV vs. SCE. To compare the data, the cathodic and anodic charge storage capacity (CSC<sub>c</sub> and CSC<sub>a</sub>, respectively) were derived by integration of the cathodic and anodic parts of the curves (**Table 1**). It can be clearly seen that the charge storage capacity increases by a factor of 3 from the bare PtIr electrode to the laser-structured electrode. The CSC of the laser-structured surface can be tuned by changing, for example, the structure depth and/or the structure density. By coating PtIr with PVD coatings or with Ampliccoat<sup>®</sup>, the CSC can be further increased by a factor of 10. In addition, the anodic and cathodic charge storage capacity values of a given electrode are in the same range, indicating that the layers do not undergo irreversible changes during the electrochemical cycles. Note that the thickness of the IrOx coating is lower than that of the other coatings, which also affects the electrochemical performance. However, IrOx coatings with thicknesses above  $1 \mu\text{m}$  have been observed to be mechanically unstable and thus are not used commercially for medical device applications.

**Table 1.** Electrical parameters of all studied electrodes with layer thickness and cathodic (CSC<sub>c</sub>) as well as anodic (CSC<sub>a</sub>) charge storage capacity values.

ELECTRODE	THICKNESS / $\mu\text{m}$	CSC <sub>c</sub> / $\text{mC cm}^{-2}$	CSC <sub>a</sub> / $\text{mC cm}^{-2}$
PtIr	n/a	$1.0 \pm 0.6$	$0.7 \pm 0.1$
Laser structured	11	$2.9 \pm 0.4$	$3.5 \pm 0.8$
TiN	$3.13 \pm 0.089$	$30.6 \pm 2.1$	$31.0 \pm 2.2$
IrOx	$\sim 0.341 \pm 0.017$	$24.0 \pm 0.9$	$23.6 \pm 0.7$
Ampliccoat <sup>®</sup>	2-3	$29.6 \pm 0.0$	$30.5 \pm 0.0$

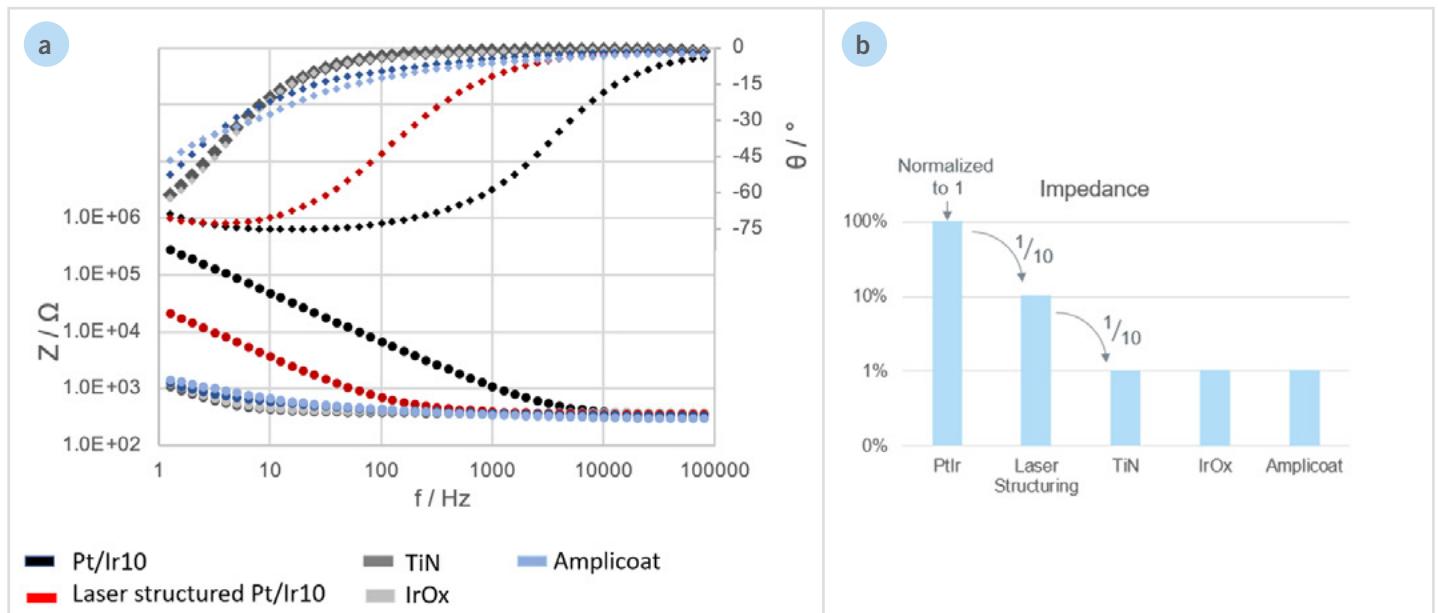


**Figure 3.** Comparison of cyclo-voltammograms and charge storage capacity of the different electrodes studied.

The CV curves also yield information regarding the mechanism of the charge transfer process. While the charge transfer mechanism is of pseudocapacitive nature for PtIr electrodes (bare and laser structured),<sup>5</sup> distinct peaks in the CV of the IrOx coated samples demonstrate a faradaic mechanism of the charge transfer process for this material.<sup>6</sup> On the other hand, a rather smooth and rectangular CV shape for TiN and Amplicoat<sup>®</sup> coated samples represents the capacitive nature of the charge transfer mechanism.<sup>5</sup> Unlike TiN & IrOx, the conductivity of Amplicoat<sup>®</sup> is a combined effect of electronic and ionic the charge transfer mechanism.

### Electrical Impedance Spectroscopy

**Figure 4** shows exemplary Bode Plots with impedance and phase data vs. frequency in the range of 1 Hz to 100 kHz. At frequencies between 1 Hz – 5 kHz, the electrodes behave capacitive, i.e., the magnitude of impedance decreases with an increase in frequency. While the bare PtIr electrodes show high impedance values of 225 kohm± 124 kohm at 1 Hz (see also **Table 2**), the impedance of laser-structured electrodes is reduced by a factor of 10 at the same frequency. With coated electrodes, the impedance is decreased further by another magnitude down to values of 1577 ± 52 Ω (IrOx), 1245 ± 84 Ω (TiN) and 1486 ± 144 Ω (Amplicoat<sup>®</sup>). This is due to an increase in double layer capacitance of these coatings which decreases its impedance at lower frequencies.



**Figure 4.** (a) Electrical impedance spectroscopy (bode plot) for all studied electrodes; (b) Comparison of impedance values of uncoated and coated Pt/Ir10.

Another determining factor for the use of surface modification is the cut-off frequency, i.e., the frequency at phase shift of 45°. As shown in Figure 4a, the cut-off frequency decreases as follows PtIr > Laser structure > TiN ≈ IrOx ≈ Amplicoat<sup>®</sup>.

**Table 2.** Electrical parameters of all studied electrodes with impedance values at  $f = 1 \text{ Hz}$ ,  $f = 10 \text{ Hz}$  and  $f = 100 \text{ Hz}$  as well as threshold frequency for a phase angle of  $\theta = 45^\circ$ .

ELECTRODE	THICKNESS / $\mu\text{m}$	$Z_{\square} / \Omega$ ( $f = 1 \text{ Hz}$ )	$Z_{\square} / \Omega$ ( $f = 10 \text{ Hz}$ ) $\square$	$Z_{\square} / \Omega$ ( $f = 100 \text{ Hz}$ )
PtIr10	n/a	225555 ± 123508	37762 ± 12773	5729 ± 1101
Laser structured	11	26544 ± 6793	3640 ± 791	674 ± 91
TiN	3-4	1245 ± 84	421 ± 29	368 ± 35
IrOx	~0.4	1245 ± 84	465 ± 9	407 ± 5
Amplicoat <sup>®</sup>	2-3	1486 ± 144	542 ± 101	248 ± 134

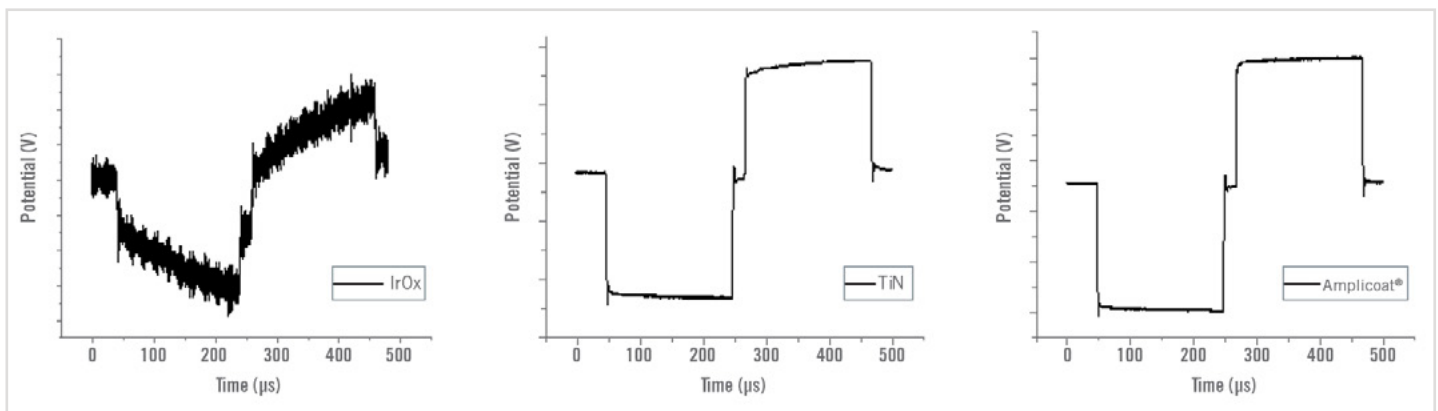
## Voltage Transient Measurements

The voltage transient graphs of IrOx, TiN, and Ampliccoat<sup>®</sup> coated Pt/Ir electrodes at a frequency of 10 Hz are shown in **Figure 5**. and show the potential response of the maximum current amplitude that can be applied safely to these electrodes without any bias. The CIC of these coatings without any applied bias functions follows the order Ampliccoat<sup>®</sup>  $\approx$  TiN  $\gg$  IrOx.

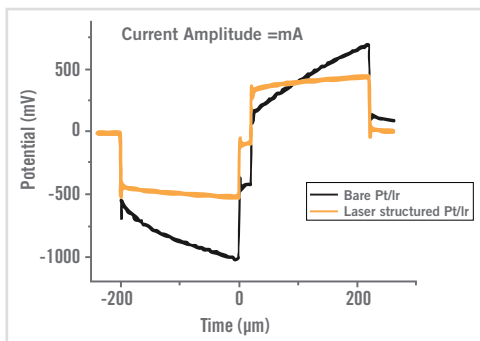
In the case of IrOx, the VT curve indicates strong polarization across the electrode-electrolyte interface. However, this behavior can be improved as shown by Ersöz et al. and Ludwig et al., where they increased the CIC of IrOx by  $>9x$  and decreased the polarization across the electrode-electrolyte interface by applying an anodic bias of 0.7 V and 0.89 V respectively. Wessling et al. and Cogan et al., in their work on Ir and IrOx, have also shown that CIC is a function of film thickness and can be increased by increasing the thickness of the coating. Thus, the charge injection capacity of an electrode coating depends on several factors, like its surface topography (rough or plain), geometrical surface area, film thickness, charge transfer mechanism, stimulation pulse width, and applied bias functions (Cogan et al., André Van Ooyen). Hence, it is not possible to conclude a single value of CIC for IrOx and other coatings, and its value should be mentioned together with the conditions under which it was measured. Therefore, the coating of interest should be reviewed in view of the specific application and the configuration of the device to draw a conclusion on its application.

TiN and Ampliccoat<sup>®</sup> show negligible polarization across the electrode-electrolyte interface. This is highly desirable for a stimulation application as it avoids unwanted reactions, thereby increasing the lifetime of the electrodes.

**Figure 6** shows the effect of an increase in the surface area of Pt/Ir electrodes and its voltage transient response at a given current amplitude. The curve in black is the VT response of a bare Pt/Ir electrode (13 mm<sup>2</sup> area), and the one in orange is the same electrode after laser structuring. Laser structuring the surface increases the GSA of Pt/Ir, thus, decreasing its polarization and increasing its charge injection capacity.



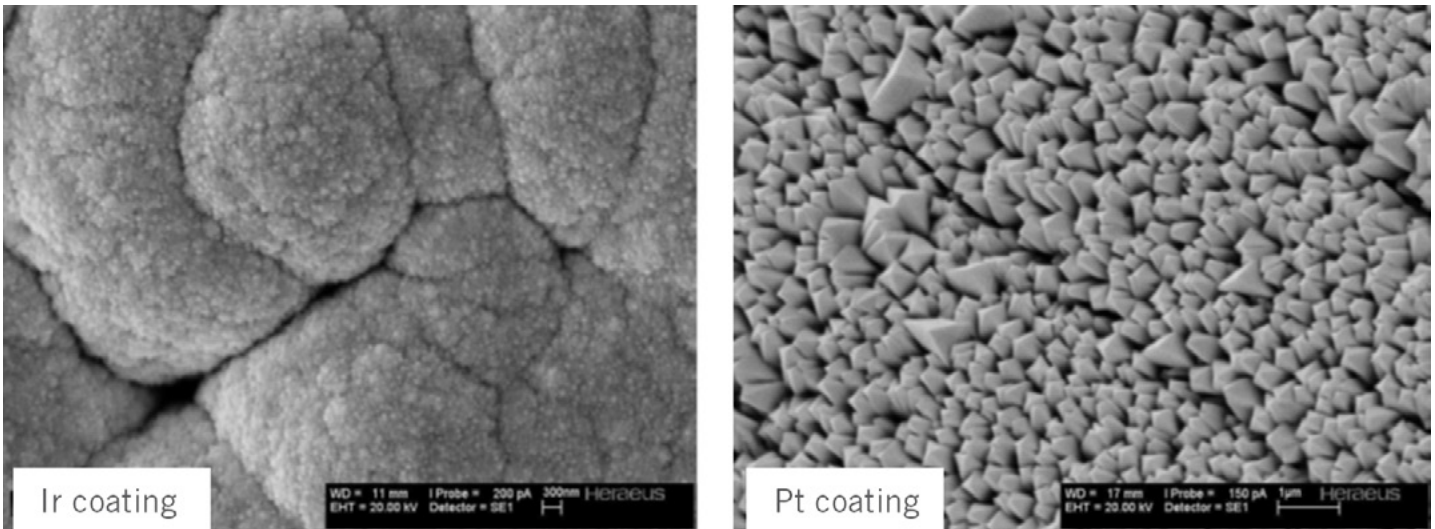
**Figure 5.** Voltage transient graph of IrOx, TiN and Ampliccoat<sup>®</sup> coating on Pt/Ir electrode, measured at a frequency of 10 Hz.



**Figure 6.** Comparison of VT curve of a bare and Laser structured Pt/Ir electrode of area 13 mm<sup>2</sup>.



In addition to TiN & IrOx, Heraeus Medevio also has expertise in other PVD coatings like Pt and Ir.<sup>8</sup> Similar to other PVD coatings, Pt and Ir coatings have an increased surface area and thus reduced impedance as compared to solid metal electrodes (SEM pics shown in **Figure 7**).

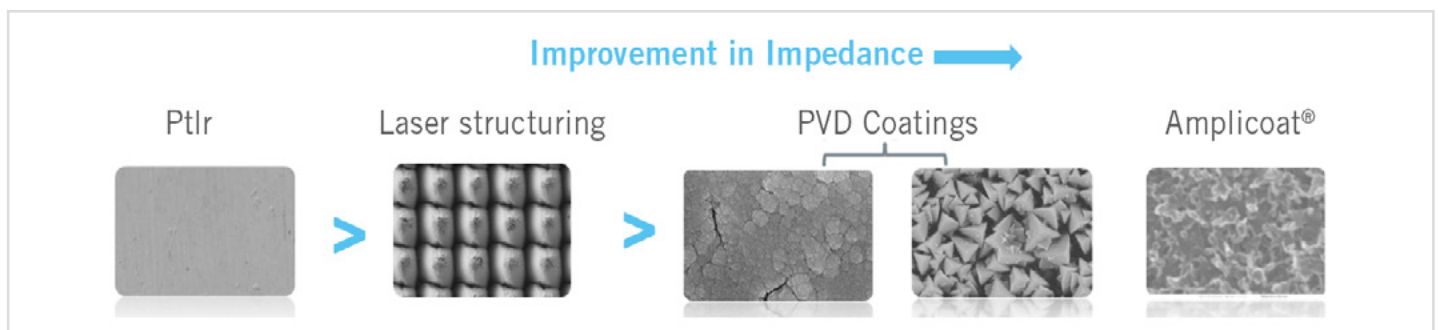


**Figure 7.** Ir coating (left) and Pt coating (right) on Pt/Ir electrode surface.

## 4. SUMMARY & OUTLOOK

In this study, we have compared the low impedance electrodes and coatings offered by Heraeus Medevio for sensing and stimulation applications. These coatings can be deposited either via PVD process or electrochemical deposition. In summary, surface modification of PtIr electrodes by laser-structuring its surface or by coating it with TiN, IrOx, or Amplicoat improves its charge storage capacity by a factor  $\geq 3$  and reduces its impedance by up to 99%. The charge injection capacity follows the order Amplicoat  $\approx$  TiN  $\gg$  IrOx  $>$  PtIr. The selection of a surface modification type can be made based on the required electrochemical property and the suitable surface modification method (**Figure 8**). This whitepaper should provide you with guidelines for selecting the right solution for your electrode application.

As mentioned in the introduction, stay tuned to learn about our other coating solutions like inkjet printed Platinum and Iridium oxide inks.



**Figure 8.** Improvement of electrochemical performance for studied electrode modifications.



# APPENDIX

## Citations

1. Ludwig, Kip A.; Langhals, Nicholas B.; Joseph, Mike D.; Richardson-Burns, Sarah M.; Hendricks, Jeffrey L.; Kipke, Daryl R. (2011): Poly(3,4-ethylenedioxythiophene) (PEDOT) polymer coatings facilitate smaller neural recording electrodes. In: *Journal of Neural Engineering* 8 (1), S. 14001. DOI: 10.1088/1741-2560/8/1/014001.
2. Norlin, A.; Pan, J.; Leygraf, C. (2005a): Investigation of Electrochemical Behavior of Stimulation/Sensing Materials for Pacemaker Electrode Applications. In: *Journal of The Electrochemical Society* 152 (2), J7. DOI: 10.1149/1.1842092.
3. Norlin, A.; Pan, J.; Leygraf, C. (2005b): Investigation of Electrochemical Behavior of Stimulation/Sensing Materials for Pacemaker Electrode Applications II. Conducting Oxide Electrodes. In: *Journal of The Electrochemical Society* 152 (7), J85. DOI: 10.1149/1.1933372.
4. Narayan, Suman; Stoica, Leonard; Liess, Andreas; Reisinger, Andreas (2021): Amplicoat<sup>®</sup>- conductive polymer coating with enhanced durability and performance for chronic implants. Proceedings of the 2021 Design of Medical Devices Conference.
5. Cogan, Stuart F. (2008): Neural stimulation and recording electrodes. In: *Annual review of biomedical engineering* 10, S. 275–309. DOI: 10 (Cogan).1146/annurev.bioeng.10.061807.160518.
6. Wilks, Seth J.; Richardson-Burns, Sarah M.; Hendricks, Jeffrey L.; Martin, David C.; Otto, Kevin J. (2009): Poly(3,4-ethylenedioxythiophene) as a Micro-Neural Interface Material for Electrostimulation. In: *Frontiers in neuroengineering* 2, S. 7. DOI: 10.3389/neuro.16.007.2009.
7. Wilks, Seth J.; Hara, Seth A.; Ross, Erika K.; Nicolai, Evan N.; Pignato, Paul A.; Cates, Adam W.; Ludwig, Kip A. (2017): Non-clinical and Pre-clinical Testing to Demonstrate Safety of the Barostim Neo Electrode for Activation of Carotid Baroreceptors in Chronic Human Implants. In: *Frontiers in Neuroscience* 11, S. 438. DOI: 10.3389/fnins.2017.00438.
8. Specht, Heiko; Krüger, Frank; Wachter, Hans Jürgen; Keitel, Oliver; Leitold, Christiane; Frericks, M. (2005): Electrochemical properties and stability of PVD coatings for the application in cardiac and neurological stimulation.
9. Thornton, John A.; Hoffman, D. W. (1989): Stress-related effects in thin films. In: *Thin Solid Films* 171 (1), S. 5–31. DOI: 10.1016/0040-6090(89)90030-8.
10. Cogan, S. F.; Plante, T. D.; Ehrlich, J. (2004): Sputtered iridium oxide films (SIROFs) for low-impedance neural stimulation and recording electrodes. In: *Conference proceedings : ... Annual International Conference of the IEEE Engineering in Medicine and Biology Society. IEEE Engineering in Medicine and Biology Society. Annual Conference 2004*, S. 4153–4156. DOI: 10.1109/IEMBS.2004.1404158.
11. Bonse, Jorn; Hohm, Sandra; Kirner, Sabrina V.; Rosenfeld, Arkadi; Kruger, Jorg (2017): Laser-Induced Periodic Surface Structures — A Scientific Evergreen. In: *IEEE J. Select. Topics Quantum Electron.* 23 (3). DOI: 10.1109/JSTQE.2016.2614183.