Electrodes or microelectrode arrays that are used for stimulation of nerve tissue and sensing or recording of neural electrical activity are the basis of emerging devices and treatments for various cardiac, neurological, retinal, and hearing disorders. They are fabricated to have very specific sizes, geometries and profiles, as well as electrical, electrochemical, and mechanical properties to match the biological requirements of their intended applications. The amount and diversity of such electrodes is vast owing to the fact that different applications demand different electrode types with respect to their size, invasiveness, selectivity, materials and performance.

In recent decades, there has been a growing need for electrode miniaturization to reduce patient trauma and induced scar tissue. Much emphasis has also been given for improvements in device performance, longevity, battery life, effectiveness, selectivity, and patient compatibility. More importantly, development of high-density microelectrode arrays to stimulate or record neural activity in various neurostimulation devices, cochlear implants, retinal prostheses, and also multi-electrode electrophysiology catheters have been the subject of many research studies. A higher density array of electrodes will allow a greater number of discrete neurons or groups of neurons to be activated and correspondingly result in increased localization and control of the desired biological response, although the minimum size of electrodes and the optimal electrode number is the subject of intense research.
In the last several decades, a multitude of research groups, startup companies, contract manufacturers, and medical device manufacturers around the globe have been working on developing neurostimulation, cardiac, electrophysiology, and cochlear devices as well as retinal prostheses with immense focus on the construction of high-density microelectrode arrays or single electrodes with enhanced electrical and electrochemical properties at their interface with the biological environment.

In general, high charge storage/injection capacity, low impedance and high capacitance electrodes and microelectrode arrays are of great interest to most device manufacturers. For most sensing, recording and stimulating applications such as deep brain stimulation and most recently in electrophysiology devices such as ultra-high-density heart mapping catheters, aiming for the best signal-to-noise ratio with the highest selectivity is critical too, thus the need to use implantable microelectrode arrays with multiple sensing, recording and stimulation sites close to the tissue. Fabrication of such electrodes, being preferably small enough for communication with single neurons, is technologically feasible considering the overall dimensions of the implant. However, a size reduction of the actual conducting site is inevitably accompanied by an increase in the impedance of the electrode, and consequently smaller electrodes will suffer from low signal-to-noise ratios and reduced charge transfer capacity due to their reduced size. The size of an electrode for clinical use is in fact determined by a trade-off between high selectivity (obtained by small size) and optimized electrochemical characteristics (obtained by electrochemically available surface area). Larger electrodes with greater geometric surface area are able to inject more charge before exceeding the electrochemically safe limits. However, larger electrodes consume greater space and as a result, limit the spatial selectivity or resolution of a device produced from such electrodes.

Generally speaking, a greater number of electrodes leads to increased geometric surface area which in turn leads to an increase in charge injection capacity and capacitance. This can inject more charge and enables the delivery of a higher resolution signal, which is expected to translate to an improvement in device performance. However, due to the space limitations within organs such as brain, spinal cord, cochlea, and eye, increasing the number of electrodes without reducing the size of the electrodes is not possible. However, reducing the size of an electrode will significantly reduce the charge which can be delivered, which again will adversely impact the device performance.

To overcome these hurdles, an alternative approach to produce a larger number of electrodes for improved selectivity and resolution but with smaller geometric surface area (GSA) is to increase the electrode electrochemical surface area (ESA). Provided that ESA can be maximized while GSA is minimized then a greater number of electrodes can be introduced into the device or in the construction of the microelectrode array, which in turn leads to increased performance and selectivity and lower power consumption and improved fidelity.

Several classes of materials and technologies have been studied and have shown to be effective in increasing ESA.

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and improving electrochemical performance of the electrodes. For example, iridium oxide coatings (IrO₂), titanium nitride coatings (TiN), black or porous platinum coatings, conductive polymers, electrochemical surface roughening, nanostructured scaffolds, two-dimensional materials, and carbon nanotubes have all been vastly studied and have shown to enhance the charge injection capacity and overall properties of electrodes and microelectrode arrays. There are major differences between these materials, technologies and their respective manufacturing techniques in terms of performance, durability, scalability, throughput, capital investment, as well as material and precious metal requirements for the manufacturing process since most electrodes are made from platinum group metals and their alloys.

Many of these techniques pose technological challenges in a manufacturing environment, e.g. their inability to employ serial or in-line processing approaches in production, the need for costly time-consuming vacuum/batch processes and the need for use of masks to selectively mask and then coat areas of interest on the electrode surface, among others. More importantly, despite the favorable electrochemical properties some of these materials and technologies offer, there are other challenges associated with the majority of them, such as poor adhesion of the coatings and additive layers to the underlying substrate or electrode surface affecting the function of the electrode, such as those reported in platinum black or IrO₂ or conducting polymers.

It is well understood that surface morphology of materials is a key factor in governing various surface properties such as optical, mechanical, wetting, chemical, biological, and electrochemical characteristics of solid surfaces. Since their invention, ultra-short pulse and femtosecond laser technology have emerged as novel and versatile technologies for producing a large variety of micro and nanostructured surfaces suitable for a wide range of applications in photonics, plasmonics, optoelectronics, biochemical sensing, micro and nanofluidics, optofluidics and biomedicine, among other areas.

**THE INVENTION**

Pulse Technologies Inc. has developed a patented technology using ultra short pulse lasers for hierarchical surface restructuring (Figure 1) of electrode materials for implantable medical device applications (Figure 2).

![Figure 1: Schematic of a hierarchically structured surface, best defined as topographic features comprised of varying length scales. For most applications, these varying length scales are the coarse-scale rough structures that are about several microns in size to a range of 10-100 microns, and a finer structure subset on top of the coarse structures in the range of about a few nanometers to 1 micron in size.](image)

**SURFACE ATTRIBUTES**

Ultrashort pulse lasers offer the unique advantage of athermal material ablation with no induced damage such as heat affected zone, micro cracking, surface debris and recast layer. This patented technology can engineer and tune surface texture and morphology (Figure 3) to increase surface roughness and available surface area to enhance electrochemical performance of the electrode by several orders of magnitude.

The hierarchical surface structures induced on the surface are comprised of varying length scales ranging from micro- to nano- structures (Figure 4 and Figure 5). This surface hierarchy greatly increases available electrochemical surface area (ESA) which in turn significantly enhances electrochemical performance of the electrode.
Figure 2: Examples of various hierarchically restructured electrodes for implantable medical device applications.

Figure 3: Scanning electron microscope micrographs of select hierarchically restructured Pt10Ir samples.

Figure 4: Scanning electron microscope (SEM) micrographs of select hierarchical surface structures induced on the surface of Pt-10Ir alloy electrodes as a result of ultrashort pulse laser restructuring.
PERFORMANCE BENEFITS

Some of the performance benefits, e.g. increase in charge storage capacity and reduction in impedance, derived from hierarchical surface restructuring of electrodes can be measured using electrochemical measurement techniques. In this work, cyclic voltammetry (CV) was used to measure charge storage capacity and Electrochemical Impedance Spectroscopy (EIS) was used to measure impedance and specific capacitance. Both CV and EIS tests were performed in a three-electrode cell (Figure 6) comprising a Ag/AgCl reference electrode, a coiled Pt counter-electrode, and identically sized electrodes using commercially available phosphate-buffered saline (PBS) solution. All potentials were recorded with respect to Ag/AgCl. All CV tests were measured at a 50 mV/s sweep rate between potential limits of -0.6 V and 0.8 V, beginning at open-circuit potential and sweeping in the positive direction first. Total charge storage capacity (CSC\text{total}) was calculated by integrating the area under the cyclic voltammagragams for a bare Pt10Ir electrode and a series of electrodes restructured under varying laser restructuring conditions (Figure 7). The voltammagrams compare electrodes restructured under various pulsing conditions by adjusting laser pulse energies to tune surface morphology and hierarchy (Figure 7, left). The CV behavior of the highest-performing hierarchically restructured electrode exhibiting the largest voltammagram is compared against a smooth Pt10Ir electrode and a 4 µm thick TiN coating (Figure 7, below). The Pt10Ir electrode exhibits distinct oxidation and reduction peaks similar to Pt electrodes. TiN voltammogram has the approximately rectangular shape expected for an electrode exhibiting only double-layer capacitance. The laser restructured Pt10Ir electrodes, on the other hand, exhibit substantially larger voltammagrams that are both semi-rectangular indicating double-layer capacitance similar to TiN, and also contain an oxidation peak at 0.8 V and a small reduction peak near 0.1 V inherent to Pt10Ir as shown in the inset CV voltammogram of Pt10Ir.
Figure 7: Cyclic voltammograms of a series of electrodes restructured under varying pulsing conditions (left), and a pristine Pt10Ir electrode and a 4 µm thick TiN coating for comparison with a laser restructured electrode (below).
Impedance was measured using EIS over a $0.1-10^5$ Hz frequency range using a 10mV root-mean-square (rms) sinusoidal excitation voltage about a fixed potential between -0.6 V and 0.8 V. All measurements were made with Gamry potentiostats and vendor supplied software. All data reported for EIS are an average of three samples per restructuring condition, tested three times, i.e. a total of nine measurements. Most notably, at frequencies below 1000 Hz, EIS tests and impedance measurements (Figure 9) exhibit approximately up to two orders of magnitude reduction in impedance for hierarchically restructured electrodes compared to pristine Pt10Ir electrodes. At higher frequencies, all electrodes exhibit resistive behavior dominated by electrolyte conductivity. Specific capacitance was calculated using EIS data and common Randles model.

SURFACE TUNABILITY

One of the advantages of hierarchically restructured surfaces compared to TiN coatings is the ability to tune the surface topography and porosity and thus engineer its ESA. TiN exhibits large CSC at slow sweep rates, but at higher sweep rates, access to all the available charge is limited by pore resistance of TiN and the tightly packed nature of the TiN pillars contrary to hierarchically restructured electrodes (Figure 8).

Use of ultra-short pulse lasers enables restructuring with various surface topographies, pore size, depth, and intercolumnar spacing to reduce pore resistance in order to increase CSC and specific capacitance as shown in Figure 7 and Figure 10. CV tests and CSC total measurements demonstrate more than 80-fold increase in total charge storage capacity (CSC total) and over 400-fold increase in specific capacitance of Pt10Ir electrodes via hierarchical laser restructuring (Figure 10). The results also demonstrate that the charge storage capacity and specific capacitance of hierarchically restructured electrodes exceed that of TiN coatings.

Figure 8: Focused ion beam (FIB) cross sections of a hierarchically restructured electrode (top) and TiN coating (bottom).
Figure 9: Impedance magnitude as a function of frequency for various hierarchically laser restructured electrodes as a function of laser pulse energy, a 4 µm TiN coated electrode and a pristine Pt10Ir electrode for comparison.
Figure 10: (left) Total charge storage capacity (CSC<sub>total</sub>) and (right) specific capacitance of various hierarchically laser restructured electrodes as a function of laser pulse energy. Included, for the sake of comparison, is also CSC<sub>total</sub> and specific capacitance of a 4 µm TiN coated electrode and a pristine Pt10Ir electrode. The CSC<sub>total</sub> is calculated by integrating the area under the cyclic voltammograms in Figure 7. Specific capacitance was calculated by the use of EIS data and common Randles model. Each data point is an average of three measurements on three electrodes, i.e. a total of nine measurements.

CONCLUDING REMARKS

Since every electrode or microelectrode array has very specific electrochemical performance requirements for an intended application, the tunability and flexibility of this technology for the design of optimal surface topographies that in turn lead to achieving such performance criteria renders ultra-short pulse laser technology a commercially viable cost-effective technology that can revolutionize the electrode, microelectrode array, and long-term implantable device markets.

Despite favorable electrochemical properties of various coating technologies, there are challenges associated with the majority of these techniques, such as poor adhesion of the coatings to the underlying substrate or electrode surface, low structural and chemical stability and poor long-term durability. In most vacuum coating technologies, undesired thermal stresses are also introduced into the coating structure, which in turn leads to durability and performance issues.

Hierarchical laser restructuring technology, on the other hand, brings numerous promises not only from a material, manufacturing and cost perspective, but also from an improved performance viewpoint, thus rendering this technology an ideal candidate for next generation sensing, recording and stimulating electrode and microelectrode array applications.

In summary, there are several advantages in using hierarchical surface restructuring technology compared to coating and thin films. In what follows, some of these benefits and advantages are outlined:

a. ultrahigh surface area and enhanced electrochemically-active-surface-area
b. ability to tune surface hierarchy by adjusting pulse and laser parameters
c. improved overall electrochemical performance
d. enhanced charge storage capacity by more than 80-fold
e. increased capacitance by more than 400-fold and reduced impedance
f. ability to integrate for serial or in-line processing in production

g. elimination of costly and time-consuming vacuum and batch processes

h. elimination of masking and similar requirements that are traditionally utilized to selectively coat areas of interest on the electrode surface

i. enhanced durability with no adhesion or delamination concerns due to lack of a secondary phase, material, or coating on the surface

j. avoidance of additional chemical procedures

k. ability to process nearly all types of materials

l. capability of processing non-planar surfaces

m. commercially viable and cost-effective due to short cycle times

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