PLATINUM-IRIDIUM COATINGS FOR INCREASING SENSITIVITY OF IMPEDANCE-BASED POLYMER MICROFLUIDIC SENSORS

A.B. Baldwin[1], C.D. Lee[2], A. Petrossians[2], J. Weiland[3], and E. Meng[1]
[1]University of Southern California, USA
[2]Platinum Group Coatings LLC, USA
[3]University of Michigan, USA

ABSTRACT

We present the first use of electrodeposited platinum-iridium (Pt-Ir) coatings for improving sensitivity and measurement range of impedance-based MEMS fluidic sensors. Pt-Ir deposited onto Pt microelectrodes increased electrochemical surface area (ESA) and decreased electrochemical impedance, enabling transduction at significantly lower frequencies (from 1 to 100 kHz) and increasing sensitivity. MEMS patency and flow sensors were characterized before and after Pt-Ir electrodeposition. Patency sensing utilizing larger electrodes exhibited moderate sensitivity gains (~3-11%), while flow sensing utilizing smaller electrodes improved significantly (61% sensitivity increase and 2x improvement in resolution (39 to 19 µm/s)). Pt-Ir coating reduced drift by an order of magnitude in flow sensors over a 12-hour period.

KEYWORDS: Platinum-Iridium, Parylene C, Electrochemical Impedance, Microfluidic Sensors, Hydrocephalus

INTRODUCTION

Impedimetric sensors monitor the electrochemical impedance between a pair of electrodes exposed to an aqueous solution, and are a promising technology for chronic *in vivo* medical devices because the sensors interact directly with physiological solutions, without needing encapsulation or protection from corrosion. Microfabricated impedimetric sensors made out of only biocompatible metals and polymers have been reported for measuring flow rate[1], fluidic pressure[2], or catheter patency[3] in the body, and we have recently developed a multi-sensor module designed for chronic implantation in hydrocephalus shunts. The frequency range available for impedimetric transduction is limited on the high end by parasitic capacitance (~100kHz) and on the low end by electrode's double-layer capacitance. For microfabricated electrodes, these frequency limits often overlap, reducing sensitivity or preventing signal transduction entirely. Increasing microelectrode ESA, such as by coating a Coulter counter with Pt black[4], has been reported to improve sensor response, and recently electroplated Pt-Ir coatings have emerged as an effective way to increase ESA in polymer neural probes[5, 6]. Here, we explored the ability of 60-40% Pt-Ir electrodeposited coatings to decrease baseline impedance, increase sensitivity and resolution, and extend measurement frequency range of an impedimetric multi-sensor module for hydrocephalus shunts.

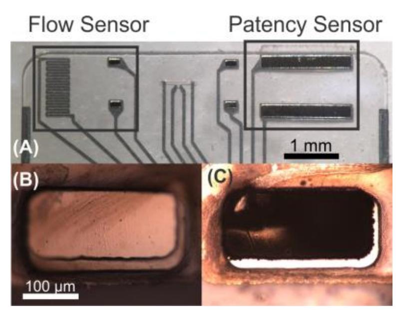

Figure 1. (A) The impedimetric multi-sensor module after Pt-Ir coating. Each module contains a flow sensor, which consists of a microfabricated heater and pair of impedance electrodes, and two electrodes which serve as a patency sensor. (B) Micrograph of a Pt flow electrode before coating and (C) after Pt-Ir coating.

METHODS

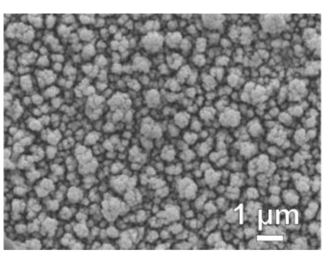

Figure 2: Representative SEM image of an electrode coated with electroplated Pt-Ir.

Platinum-Iridium Coating

Electrodeposition of Pt-Ir was performed by Platinum Group Coatings, LLC using previously reported methods involving ultrasonication and voltage cycling in solution containing Na_3IrCl_6 and Na_2PtCl_6[5]. Electroplated Pt-Ir exceeds the performance of Pt black; Pt-Ir coatings are highly fractal and exhibit pseudo-capacitive reactions, dramatically increasing ESA and significantly improving neural electrodes. Pt-Ir's biocompatibility and room-temperature coating process makes it a promising candidate for polymer sensors, implantable devices, and microfluidics.

Sensor Design

We applied Pt-Ir coatings to multi-sensor modules containing microfluidic patency[3] and flow[1] sensors. These flexible sensors are fabricated from 2000Å Pt sandwiched between two 10µm Parylene C layers and are intended to transduce blockage and flow through hydrocephalus shunts. Sensors utilize electrochemical impedance between electrode pairs exposed to cerebrospinal fluid. The flows sensor operates by delivering a heat pulse to physiological fluid using a microfabricated heater and measuring the pulse's time of flight as it travels past one or more pairs of impedance electrodes;

the patency sensor directly measures the impedance across electrodes inside and outside a catheter, and partial catheter occlusion will cause the impedance magnitude to increase. A pressure sensor is also included on the multi-sensor module, but pressure sensor tests after Pt-Ir coating are still ongoing.

Benchtop Testing

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on electrodes before and after coating. For benchtop testing, devices were packaged into modules compatible with standard hospital catheters (ID 3.25 mm). To test the patency sensor, catheters with varying number of holes (simulating progressive blockage) were attached and filled with saline. EIS was performed through each catheter between the coated electrode and an uncoated Pt wire placed external to the catheter. For flow testing, a syringe pump was used to control saline flow, and impedance was recorded using an Agilent LCR meter.

RESULTS

Robust Pt-Ir coating was achieved on multiple devices containing flow and patency sensors. CV and EIS revealed a dramatic decrease in electrode impedance magnitude and absolute value of phase (81x magnitude decrease and 65° phase increase at 100Hz), and a 17.9x increase in charge storage capacity in saline. Patency sensor testing revealed only a small decrease in baseline impedance, due to patency impedance consisting mainly of resistance through the catheter which is not dependent on electrode surface area, and an increase in sensitivity (3.59% for electrode 1 and 11.1% for electrode 2) after coating. Flow sensor testing revealed a dramatic 61.2% increase in sensitivity after coating and an improvement in 2σ resolution from 38 to 19 μm/s. Furthermore, the frequency range available for flow transduction was extended down to 1 kHz, while 100 kHz was necessary for uncoated sensors. Pt-Ir also increased sensor stability and reduced flow sensor drift over a 12 hr period from 2.1%/hr pre-coating to less than 0.16%/hr post-coating.

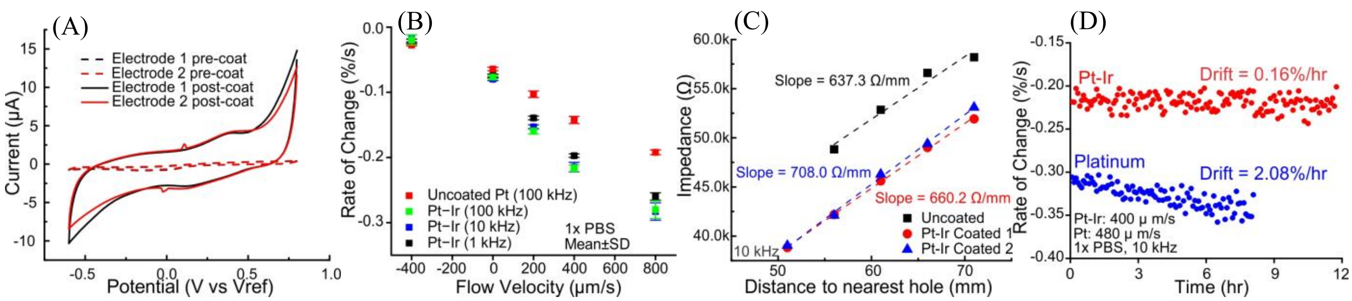

Figure 3. (A) Cyclic voltammetry before and after Pt-Ir coating reveals a 17.9x increase in charge storage capacity in phosphate-buffered saline (0.21 to 3.7 μC). (B) Flow sensors coated in Pt-Ir increased sensitivity 61.2%, from $-1.4x10^{-4}$ to $-2.3x10^{-4}$ %/μm/s, 2σ resolution improved from 38 to 19 μm/s, and flow transduction was possible at lower frequencies (down to 1kHz) for the first time. (C) Patency sensor improvement after Pt-Ir coating was minimal, due to the already large size of the patency electrodes. (D) Sensor drift also improved, dropping from nearly 2% per hour to negligible.

CONCLUSION

Pt-Ir coatings significantly improve MEMS fluidic sensors and will enable further miniaturization of polymer MEMS sensors and implantable devices. Future work will evaluate additional impedance-based sensors as well as Pt-Ir longevity and *in vivo* use.

REFERENCES

1. Baldwin, A., L. Yu, and E. Meng, *An Electrochemical Impedance-Based Thermal Flow Sensor for Physiological Fluids.* Journal of Microelectromechanical Systems, 2016. **25**(6): p. 1015-1024.
2. Yu, L., C.A. Gutierrez, and E. Meng, *An Electrochemical Microbubble-Based MEMS Pressure Sensor.* Microelectromechanical Systems, Journal of, 2016. **25**(1): p. 144-152.
3. Kim, B.J., et al., *Parylene MEMS patency sensor for assessment of hydrocephalus shunt obstruction.* Biomedical microdevices, 2016. **18**(5): p. 87.
4. Zheng, S., M. Liu, and Y.-C. Tai, *Micro coulter counters with platinum black electroplated electrodes for human blood cell sensing.* Biomedical microdevices, 2008. **10**(2): p. 221-231.
5. Petrossians, A., et al., *Electrodeposition and characterization of thin-film platinum-iridium alloys for biological interfaces.* Journal of The Electrochemical Society, 2011. **158**(5): p. D269-D276.
6. Petrossians, A., et al., *Improved Biphasic Pulsing Power Efficiency with Pt-Ir Coated Microelectrodes.* MRS Proceedings, 2014. **1621**: p. 249-257.