Potential applications of a small and high surface area Platinum electrode as an implanted impedance bio-sensor or recording electrode

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ABSTRACT

A small Platinum (Pt) electrode (geometric area: ~0.43 mm^2) was treated in an electrochemical etching process, to produce a highly porous columnar thin layer (~600 nm) on the surface of the electrode. The modified Pt electrode (Pt-p) showed similar electrical properties to a platinum-black electrode but with high mechanical integrity. Previous studies of chronic stimulation had also shown good biocompatibility and surface stability over several months implantation.

This paper discusses the potential applications of the modified electrode as an implanted bio-sensor: (1) as a recording electrode compared to an untreated Pt electrode. (2) as a probe in detecting electrical characteristics of living biological material adjacent to the electrode *in vivo*, which may correlate to inflammation or trauma repair.

Results of electrochemical impedance spectroscopy (EIS) revealed much lower electrode interface polarisation impedance, reduced overall electrode impedance, and a largely constant impedance above 100 Hz for the Pt-p electrode compared with untreated Pt electrodes. This provides a platform for recording biological events with low noise interference. Results of A.C. impedance spectroscopy of the high surface area electrode only reflect changes in the surrounding biological environment in the frequency range (1 kHz to 100 kHz), interference from electrode polarisation impedance can be neglected.

The results imply that the surface-modified electrode is a good candidate for application to implantable biosensors for detecting bio-electric events. The modification procedure and its high surface area concept could have application to a smart MEMS device or microelectrode.

Keywords: Implanted electrode, Bio-sensors, Neural recording electrode, Electrochemical impedance spectroscopy (EIS), Bio-impedance, Cochlear implant, Surface modification.

1. INTRODUCTION

Development of implantable bio-sensors, such as cell-based sensors (Jung, Cuttino et al. 1998), and extracellular neuronal activity sensors (Nisch, 1994) is an important field of research for implantable prosthetics. In particular, the use and advantages of surface-modified Platinum electrodes (Pt-p) in recording potential changes and monitoring bio-impedance *in vivo* is deserving of study.

A recording electrode for medical and biological applications requires low electrode-electrolyte impedance and a stable electrode potential to ensure a satisfactory signal-to-noise ratio (Geddes 1972, Regan 1989). For microelectrodes used in the recording of physiological events such as nerve signals *in vivo*, a platinizing process is often employed to lower the interface polarization impedance. This also gives a more stable electrode potential as compared to that of a noble metal electrode. Jung (1998) reported that platinizing resulted in an impedance reduction from 60 MΩ to 1 MΩ at 100 Hz, whereas Nisch (1994) reported reductions from 4 MΩ to 0.4 MΩ at 1 kHz. However, the electrodes employed in these studies do not suit implantable applications due to doubts about their stability in a living body.

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A neural prosthesis often must fulfil two functions: one being to deliver processed electric signals to peripheral nerve fibres; the other to record the neural cell responses and other biological events. In the case of cochlear implants, the implant converts acoustic signals into parameters of an electrical stimulus which results in auditory nerve impulses, lead to the perception of sound by the user. The principal function of the cochlear implant is to partially restore hearing function for people with profound sensorineural hearing loss (Patrick and Clark, 1991). The Nucleus 24 Cochlear Implant System can also record neural response (Abbas, Brown, 1999) and electrode impedance (Busby, 2000) through a telemetry function Current research intiatives are evaluating whether increased numbers of smaller-sized electrodes might be a means to improving sound coding (Clark, 1999). Therefore, the outcomes of this study are significant and meaningful for the further development of the cochlear implant.

Recently, we investigated a surface-modified Pt electrode as a candidate for cochlear implant application. This electrode showed good bio-compatibility and surface stability in an animal model over several months implantation (Liu et al., 2000;, Tykocinski et al., 2000]. Its frequency-dependent impedance characteristics clearly suggest that it also can be a good candidate as an implanted electrode probe for potential recording and bio-impedance monitoring.

It should be pointed out that most investigations of the impedance behaviour of platinized microelectrodes are conducted *in-vitro*. That approach is not able to include the effect of tissue response on electrode impedance characteristics. In this study, the electrode impedance characteristics of intracochlear Pt electrodes were monitored in real time while implanted in the cochleas of cats. The electrodes were surface-treated to produce a stable porous columnar thin layer, and electrode impedances were compared before and after the surface treatment. The frequency dependent impedance was studied with Electrochemical Impedance Spectroscopy (EIS). The advantage of the modified Pt electrodes in the application of recording electrodes and bio-impedance probes is discussed. The results could apply to other surface modifications in a MEMS-fabricated device.

2. EXPERIMENTAL METHODS

1. Animals and Surgery

Twelve normal-hearing adult cats were each bilaterally implanted with intracochlear electrode arrays. Five cats were implanted with normal Pt electrodes and the other seven cats were implanted with surface modified Pt electrodes. Surgery was performed under sterile conditions. The details of the surgical procedure were similar to those reported previously (Xu, Shepherd et al. 1997). The care and use of animals reported in this study was approved and conducted under the The Royal Victorian Eye and Ear Hospital's Animal Research Ethics Committee Guidelines.

2. Intra-cochlear Electrodes

The normal Pt electrodes (Pt)

The normal intra-cochlear electrodes consisted of Platinum (Pt) rings of 0.3 mm width on a Silastic MDX-4-4210 carrier. The geometric surface area of each electrode was approximately 0.43 mm^2, and the inter-electrode separation was 0.43 mm. Teflon insulated platinum-iridium (90:10) wires connected each Pt electrode to an insulated, multistranded stainless-steel lead wire. The stainless steel lead wire system provided external access to the electrodes for impedance measurement.

Surface modified porous Pt Electrodes (Pt -p)

The normal Platinum intra-cochlear electrodes were treated with an electrochemical etching process in 1 M H_2SO_4 (Real, 1992; Pajkossy, 1994). This treatment produced a stable porous columnar thin layer approximately 600 nm thick on the surface, which provided high surface area when in contact with saline or body fluid. Thus the modified Pt electrode had the same geometric area as the normal Pt electrodes but much greater real surface area. The two types of electrode are referred as Pt (normal Pt) and Pt-p (porous Pt) in this paper.

3. Electrochemical Impedance Spectroscopy (EIS)

EIS was performed with an Electrochemical interface (Solartron, Model SI 1287) and an Impedance Gain-Phase Analyser (FRA) (Solartron, Model 1260). All impedance scans were run in two-electrode configuration at the equilibrium potential (open circuit potential) using the 10 mV A.C. sine signal. All data were integrated over five cycles. The current was restricted to 20 microamperes by a cut off mode in the instrument. The test signal was scanned in the frequency range 100 kHz to 1 Hz. EIS was conducted immediately following implantation surgery. The impedance measurement was made in regular intervals for several months post implantation. Each measurement took approximately half a minute.

3. RESULTS AND DISCUSSION

1. Frequency impedance characteristics *in vivo*

Typical impedance spectra of the electrodes are given in Figure 1. The values shown in the hollow symbols were measured immediately following surgery. It is obvious that the impedance of the Pt-p electrodes is much lower than the untreated Pt electrodes from approximately 1000 Hz onwards to the low frequency end (Figure 1 a). The impedance was not much different at 10 kHz to 100 kHz, as the electrodes were the same size and were in contact with body fluid. In the high frequencies, impedance is relatively low and dominated by the resistive component shown by the low phase angle in Figure 1 b. After two weeks, the impedance increased because of tissue response or an inflammatory response, which altered the resistance of biological substances adjacent to the electrodes. However, the proportion of the increase in impedance magnitude is only large at the high frequency range; it is minor in the low frequencies from 1000 Hz down. This tendency is more obvious in Figure 1 c in which the linear scale of impedance is used.

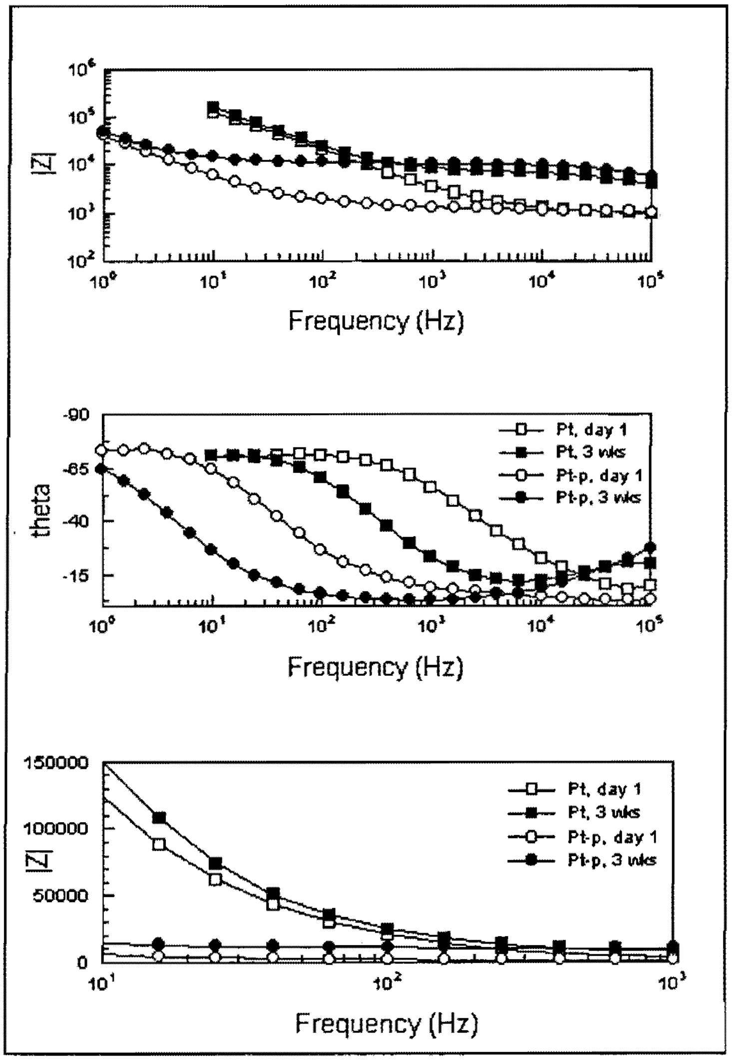


Figure 1: Typical impedance spectra of Pt electrode with and without the surface treatment following surgery immediately (day 1) and three weeks later (3 weeks.); Circle: treated Pt (Pt-p), Square: untreated Pt (Pt). (a) Impedance magnitude (ohm) versus frequency; (b) Phase shift versus frequency; (c) Linear impedance magnitude (ohm) plot between 10 Hz to 1000 Hz.

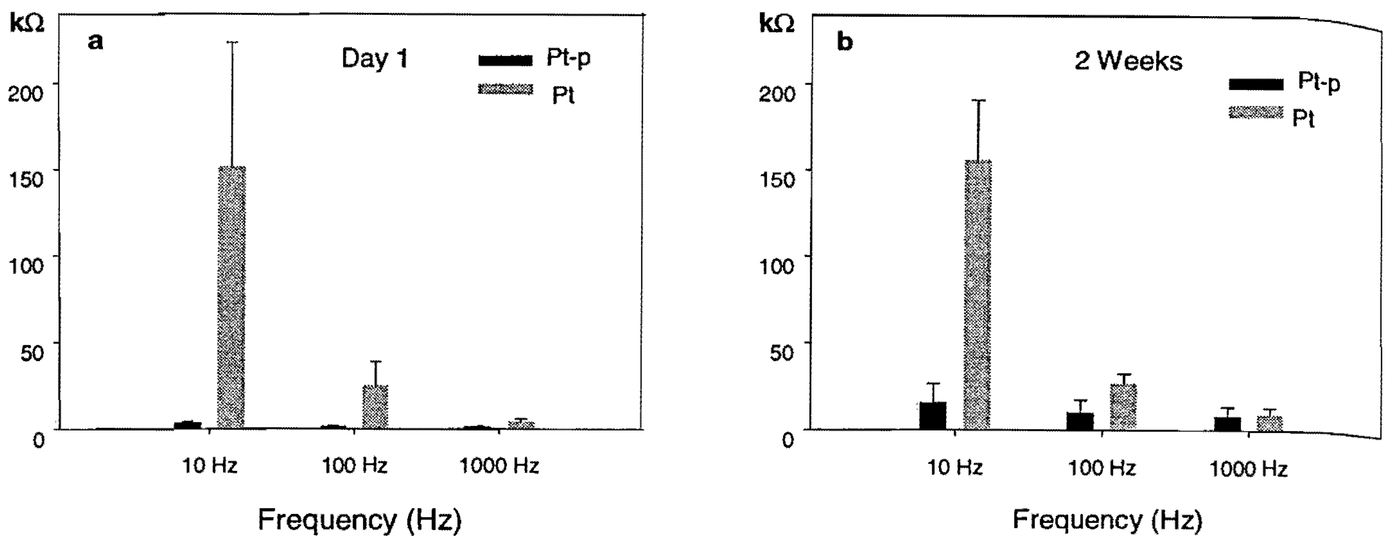


Figure 2: Comparison of magnitude of impedance between treated electrodes (Pt-p, n=7)) and untreated electrodes (Pt, n=5) at (a) following surgery; (b) two weeks later.

Figure 1.c clearly reveals the effect of the Pt-p electrode in reducing the impedance across the entire frequency range from 10 Hz to 1000 Hz, which is relevant for nerve signal recording (Blau, 1997). The group data (Figure 2) of Pt-p electrodes and Pt electrodes further verifies the significant reduction of impedance in the low frequency region. This indicates that the advantage of the Pt-p electrodes in potential recording is retained even with the presence of tissue response. It is therefore a good candidate as an implant recording electrode.

2. Advantage of surface modified Pt electrode in signal recording

An approximate equivalent circuit for biological recording electrodes is suggested as Z_A or Z_B in Figure 3. Z_A includes the resistance of metallic parts R_m, electrolyte resistance R_s and electrode-electrolyte interface impedance. The interface impedance consists of a series combination of resistance and capacitance, but the value of each is frequency dependent (Geddes, 1972, Schwan, 1992). EIS data is consistent with the model, but the impedance phase angle approaches only 75 degrees instead of 90 degrees (Figure 1.b). R_m is neglected for the cochlear electrodes. To simplify the circuit, a series connection of access resistance R_a and double layer capacitance C_{dl} is used (Figure 3.b), which reflects the impedance contribution from biological substances (electrolyte) and electrode interface polarization.

The entire electrode impedance $Z_E = R_a - j\,\dfrac{1}{\omega C}$

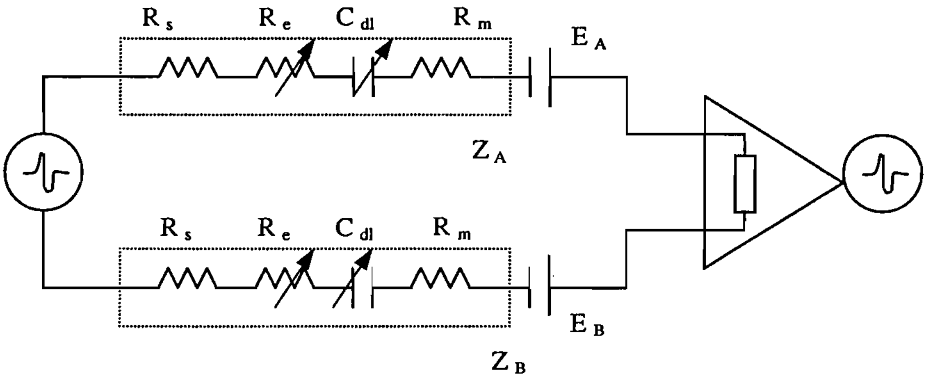
where j is the imaginary unit $j = \sqrt{-1}$, $\omega = 2\pi f$, ω angular frequency, radian /second; f, frequency, Hz.

The Pt-electrode leads to the low impedance because of its high surface area, which results in high double layer capacitance C_{dl}. The effect of the increase in surface area on the frequency dependent impedance component becomes important as the frequency decreases.

According to the simplified circuit in Figure 3.b, $E_s = E_s^* + I Z_E = I Z_{in} + I Z_E$

$$E_s^* / E_s = 1 - Z_E / (Z_{in} + Z_E)$$
$$E_s^* / E_s = Z_{in} / (Z_{in} + Z_E)$$

Therefore, when $Z_E << Z_{in}$, $E_s^* \approx E_s$. It is explicit that small electrode impedance Z_E and a large amplifier input impedance Z_{in} provide the best coupling of the signal. Moreover, a more stable and identical half cell potential E_A and E_B result with the high surface area electrode *in vivo*. It should be emphasized that the advantage of the surface modification demonstrated here is on 0.43 mm^2 Pt electrodes. Its benefits can be more pronounced when the electrodes become smaller to the micron scale.



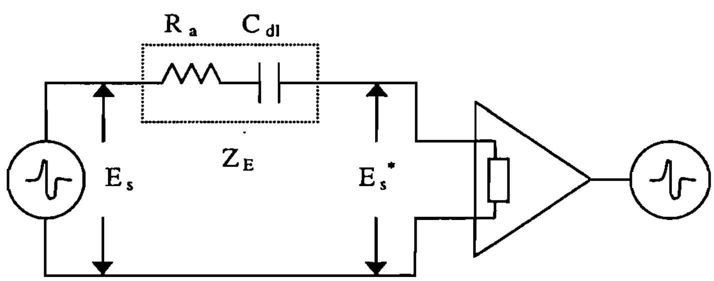


Figure 3: Simple equivalent circuit of two recording electrodes and amplifier (a); Z_A and Z_B represent two identical Pt electrodes; R_m is the resistance of the metallic portion of the electrode; R_s is the resistance of body fluid and tissue surrounding the electrode; R_p and C_{dl} are the electrode double layer resistance and capacitance which depend on frequency. Z_{in} is the input impedance of the amplifier. E_A and E_B are the half cell potentials; (b) Further simplified equivalent circuit of recording electrodes and the amplifier. Z_E is the total electrode impedance; R_a is the resistance of body fluid or tissue; C_{dl} is the electrode double layer impedance. E_s is the real potential signal, E_s^* is the recorded potential by the amplifier.

3. Bio-impedance probe

Bio-electrical impedance measures provides useful information on biological tissue structure and physiological events (Ackmann and Seitz, 1984). For implanted electrodes such as intracochlear electrode arrays, the bio-impedance may correlate with inflammation or fibrous tissue growth around the electrode. This biological effect should be understood and minimised. By using a small electrode or a micro-electrode, the local biological environment and its coupling with the electrode can be investigated. However, electrode polarization impedance could be a major artifact over a much wider frequency range. Some researchers have suggested separation of the current probe and potential probe to eliminate this problem (Kinouchi, 1997).

Use of Pt-p electrodes allowed bio-impedance measurement to be extended across a wider frequency range, from 10 kHz – 100kHz to 1 kHz –100 kHz. This is shown clearly in Figure 4. The characteristic frequency (1 k for Pt-p, 10 k for Pt) are indicated by the arrow at which electrode polarization impedance starts to increase rapidly and becomes a dominant contribution to total electrode impedance (Figure 4). The high surface area Pt-p electrode provides a wider frequency range for investigation of bio-impedance characteristics.

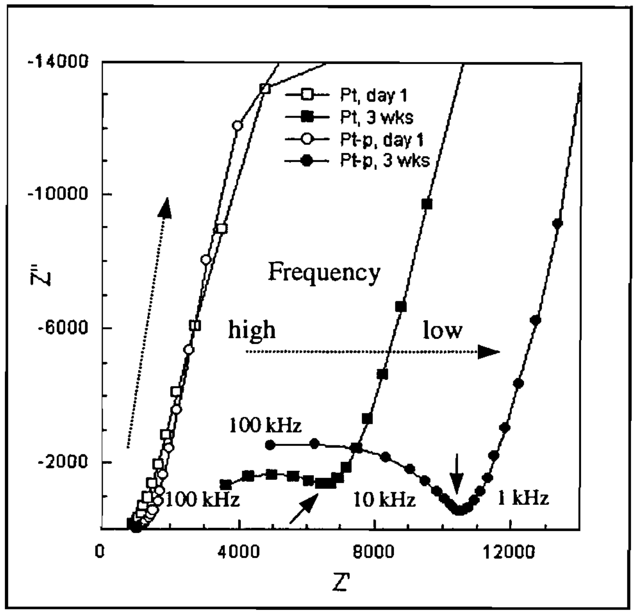


Figure 4: Complex impedance plot (imaginary impedance Z" versus real impedance Z') of the treated Pt electrodes (Pt-p) and untreated Pt electrodes (Pt) following surgery (hollow symbol) and three weeks later (solid symbol). The characteristic frequency is 1 kHz for Pt-p, and 10 kHz for Pt.

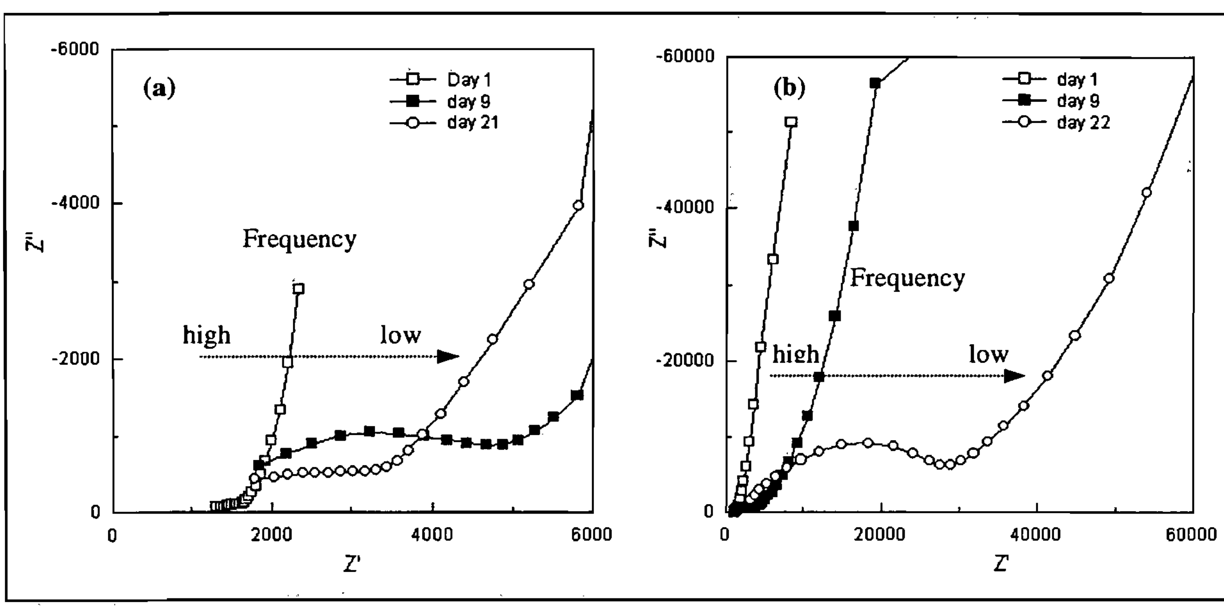


Figure 5: Complex impedance plot (imaginary impedance Z" versus real impedance Z') of the treated Pt electrode (Pt-p) at post implantation for two individual animal subjects (a) and (b). The unit is ohm but the scale in (b) is ten times larger than the scale in (a).

Figure 5 shows EIS spectra measured over 3 weeks following implantation in two cats. The changes in bio-impedance spectra over time are shown as changes in the locus at high frequency range, and this may correlate to a tissue response mechanism. Individual living cells are surrounded by a membrane having a typical capacitance value of 1 $\mu F/cm^2$. The interior of the cell contains cytoplasm having a typical resistivity on the order of 300-400 ohm-cm, whereas tissue fluid containing electrolytes has resistivity in the order of 50 ohm-cm. The resistivity of perilymph in the scala tympàni is 70 ohm-cm. Therefore, the shape and relative position of the spectra at high frequency down to 1 kHz could imply the types and numbers of the cells, and give an insight into the bio-impedance we are currently studying. The impedance magnitude at 1 kHz of the two animals in Figure 5 that reflects the bio-impedance is listed in Table 1. The impedances show large differences in the magnitude and changes over time.

Day	Subject A (kΩ)	Subject B (kΩ)
1	1.66	1.38
9	4.96	4.41
21*	3.49	23.3

Table 1: Magnitude of impedance at 1 kHz (bio-impedance) of the two subjects in Figure 5. * 22 days for Subject B.

4. SUMMARY AND OUTLOOK

This *in vivo* study demonstrated the potential use and advantages of surface treatment in implantable recording electrodes and bio-impedance probes. The investigation was carried out using large intracochlear electrodes, but the benefits of the surface modification will be more pronounced with micro-electrodes, where electrode polarization becomes obvious. The study suggests that not only the specific treatment used, but also the concept of high real surface area or other electrochemical super-capacitance materials, could be incorporated into an implantable bio-sensor device fabricated using MEMS technology. Advanced technologies such as nano-technology also provide us many opportunities.

5. ACKNOWLEDGMENT

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