Fabrication and Electrochemical Comparison of SIROF-AIROF-EIROF Microelectrodes for Neural Interfaces

Xiao-Yang Kang, Jing-Quan Liu*, Hong-Chang Tian, Bin Yang, Yanna NuLi and Chun-Sheng Yang

Abstract— **Iridium oxide has been widely used in neural recording and stimulation due to its good stability and large charge storage capacity (CSC). In general, the iridium oxide film used in the electrophysiological application can be grouped into three principal classifications: sputtering iridium oxide film (SIROF), activated iridium oxide film (AIROF) and electrodeposited iridium oxide film (EIROF). Although these kinds of iridium oxide all can remarkably reduce the impedance and increase the CSC of the microelectrode, they also exhibit markedly differences in electrochemical performances. After activation, the CSC of EIROF is 68.20 mC/cm^2, which is 88.7 % larger than that of the SIROF and 67.6 % larger than that of the AIROF. The impedance at 1 kHz of the three kinds of iridium oxide microelectrode is around 4000 ohm, it is acceptable for the neural interface application. The phase at 1 kHz of the AIROF microelectrode is the largest which is - 6.1 degree, about 22.6 % of the SIROF and 44.5 % of the EIROF.**

I. INTRODUCTION

MEMS based microelectrodes have been modified by the polydopamine added platinum black (pDA-PtBK) to achieve better mechanical stability, compared to the platinum black only (PtBK) reported at EMBC 2013 [1]. Although platinum black modified microelectrodes have been used in impedance reduction, iridium oxide is more widely used due to its good stability and large charge storage capacity (CSC) for neural recording and stimulation. A lot of fabrication methods for iridium oxide film were reported, such as sputtering iridium oxide film (SIROF) [2], activated iridium oxide film (AIROF) and electrodeposited iridium oxide film (EIROF) [3]. Seeking the best electrochemical performance and simplest fabrication method of iridium oxide film is of key impact on the neural interfaces. Here, we have fabricated three kinds of microelectrodes modified by SIROF, AIROF and EIROF, respectively. The electrochemical performances and fabrication methods are compared to find out the most suitable iridium oxide for the application of neural interface.

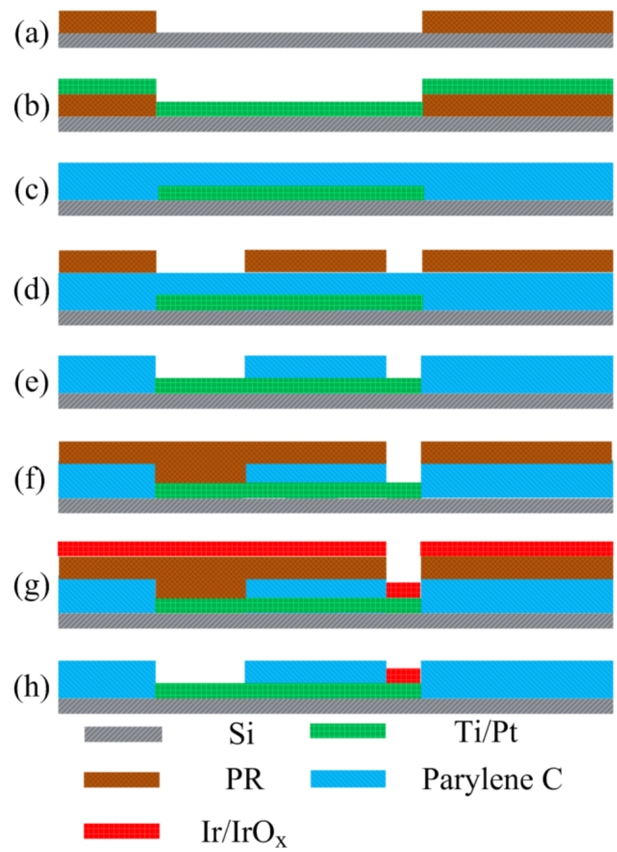

Figure 1. Fabrication process of the microelectrodes for neural interface. (a) Photoresist spin coating and patterning, (b) Ti/ Pt layer sputtering and patterning, (c) CVD Parylene C, (d) Photoresist spin coating and patterning, (e) RIE open microelectrode site, (f) Photoresist spin coating and patterning, (g) Ir or IrO$_x$ layer sputtering, (h) Ir or IrO$_x$ layer patterning.

II. EXPERIMENTAL DETAILS

Fig. 1 shows the fabrication process of the microelectrodes for neural interface. At first, a 5 µm thick positive photoresist (PR) layer was spun and patterned on the silicon wafer (3 inches in diameter, 100 crystal orientation), as shown in Fig. 1(a). Next, a Ti adhesive layer and Pt thin film were sputtered and patterned by a lift-off process (Fig. 1(b)). Then, 5 µm thick Parylene-C film was deposited on the silicon wafer by the chemical vapor deposition (CVD) process (Fig. 1(c)). A 10 µm thick PR was spun and patterned (Fig. 1(d)) to define the microelectrode site and bonding pad. After that, the microelectrode site and bonding pad were formed by a reactive ion etching (RIE) system (Fig. 1(e)). A 5 µm thick PR was spun and patterned (Fig. 1(f)) to define the

This work was supported by the National Natural Science Foundation of China (Nos. 51035005 and 61076104), 973 Program (2013CB329401), Shanghai Municipal Science and Technology Commission (Nos. 13511500200 and 11JC1405700), National Defense Pre-Research Foundation of China (Nos. 9140A26060313JW3385), HF Key Lab (HF2012-k-01), WUXI-SJTU project (2011JDZX017), SJTU-Funding (YG2012MS51).

Xiaoyang Kang (e-mail: xykang@sjtu.edu.cn), Jingquan Liu (phone: +86-021-34207209; e-mail: jqliu@sjtu.edu.cn), Hongchang Tian (e-mail: hchtian@sjtu.edu.cn), Bin Yang (binyang@sjtu.edu.cn) and Chunsheng Yang (csyang@sjtu.edu.cn) are with the National Key Laboratory of Science and Technology on Micro/Nano Fabrication, Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Department of Micro/Nano Electronics, School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China.

Yanna NuLi is with the Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China (e-mail: nlyn@sjtu.edu.cn).

978-1-4244-7929-0/14/$26.00 ©2014 IEEE

microelectrode site. Then, a 300 nm Ir or IrO_x layer were sputtered (Fig. 1(g)) and patterned by a lift-off process (Fig. 1(h)). The IrO_x layer was used for the SIROF; the Ir layer was used for the AIROF. For the EIROF, the Fig. 1(f-h) was not needed. The fabricated microelectrode site was shown in Fig. 2. The diameter of the microelectrode site was 100 μm.

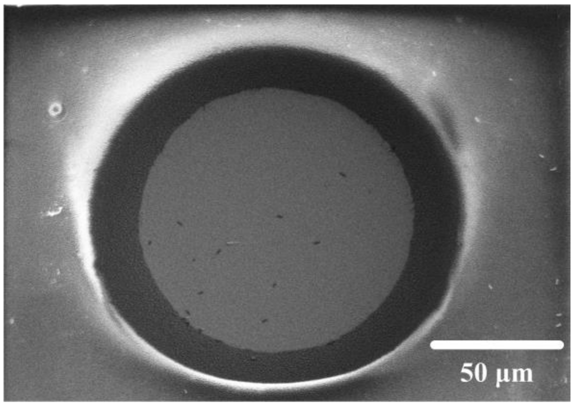

Figure 2. SEM of the fabricated microelectrode site.

A. SIROF

A Nichiden Anelva, SPF-210H sputtering equipment was deployed to deposit SIROF. Based on our previously study [4], the optimal condition of SIROF deposition is that the oxygen flow is 25 sccm and the Ar flow is 10 sccm. The sputtering pressure is 4.2 Pa and the pressure ratio between O_2 and Ar pressure is 3:4. The transformation of iridium and oxide atoms during the fabrication process of SIROF is shown in Fig. 3(a); they are directly forming the SIROF in plasma atmosphere.

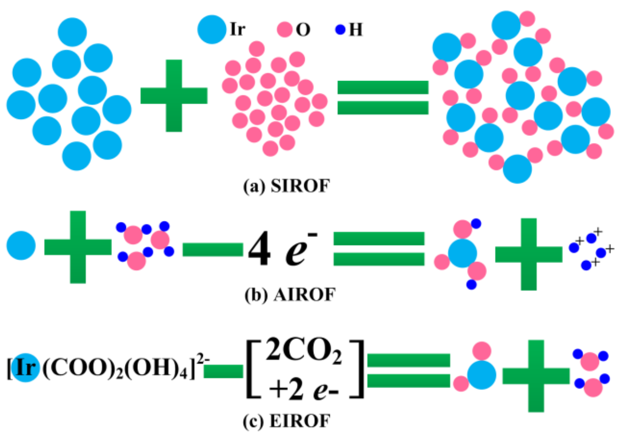

Figure 3. Fabrication process of the SIROF, AIROF and EIROF.

B. AIROF

The AIROF microelectrodes could be easily fabricated only by a potential or current sweeping and pulsing from the iridium microelectrodes. Based on our previously study [5], the AIROF was activated in physiological saline solution (0.9 % NaCl) from iridium film at pH=7. For one activation cycle, the potential is swept from −1.0 to 1.0 V at 0.05 Hz. The transformation of iridium and oxide atoms during the fabrication process of AIROF is shown in Fig. 3(b), the iridium atoms and the water molecules are forming the $IrO(OH)_2$. After 500 activation cycles, all the iridium has been activated to Ir (IV) to form the AIROF.

C. EIROF

The EIROF was fabricated by an electrodeposition process from a solution containing a suitable iridium complex. In this work, a 100 mL solution containing 75 mg portion of iridium tetrachloride, 0.5 mL aliquot of aqueous 30% hydrogen peroxide solution, 250 mg of oxalic acid was used. The pH was adjusted to 10.5 by adding small portions of anhydrous potassium carbonate. It needs to sit quiescently for 48 h before electrodeposition. An anodic deposition of EIROF was created by cycling 200 times at 0.0 V and 0.6 V for 12 second. The transformation of iridium and oxide atoms during the fabrication process of EIROF is shown in Fig. 3(c). There are two stages in the electrodeposition process as shown in Fig. 4(a).

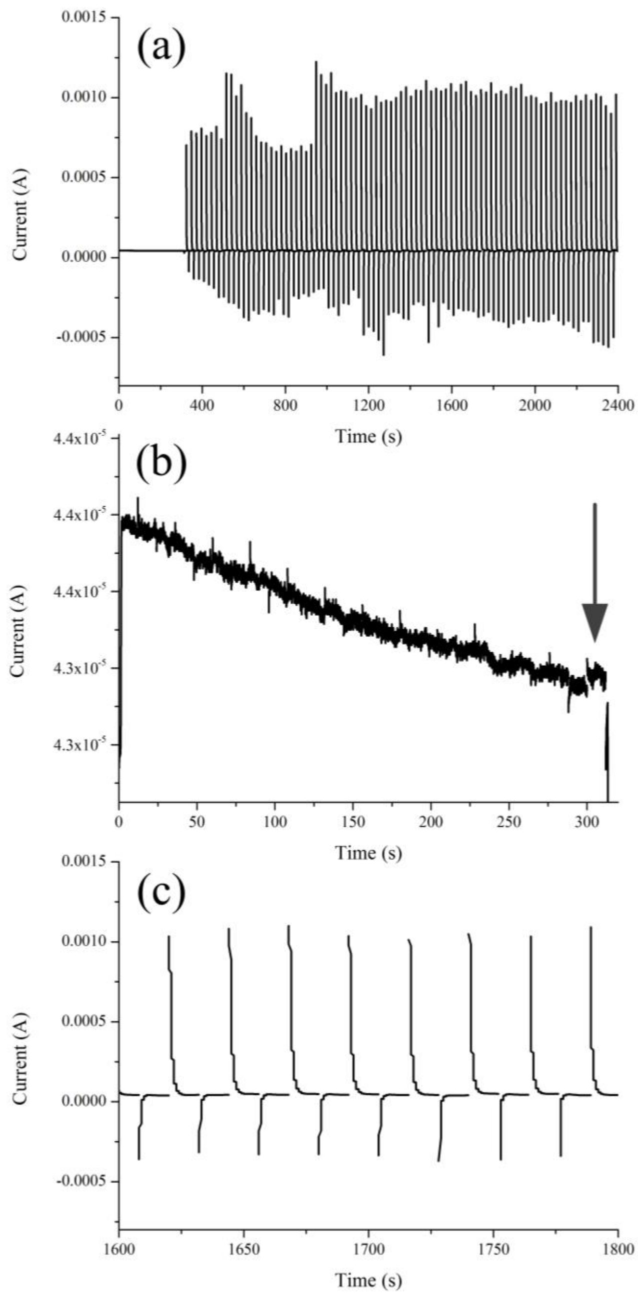

Figure 4. The current- time curves during the anodic deposition of EIROF.

At the first 26 cycles, the seeds of the EIROF are deposited on the microelectrode site as shown in Fig. 4(b). The arrow shows the accomplishment of this process. Then the seeds keep to growing EIROF and the current is much larger than the first 312 second, which is shown in Fig. 4(c).

D. Electrochemical measurement

The electrochemical measurement was proceeded in a physiological saline solution (0.9% NaCl) by the standard three electrodes system with an Ag/AgCl reference and a Pt-sheet counter electrode. The CSC of the microelectrode was determined by the cyclic voltammetry (CV) in the same electrochemical cell. After 100 activation cycles, 6 cycles were collected for each CV curve, with a potential range of −0.6 to 0.8 V to keep the voltage in the "Water Window" region. The CSC of the iridium oxide microelectrode was measured at a scan rate of 100 mV/s. The electrochemical impedance spectroscopy (EIS) was examined at the same time. The sinusoidal signal had the amplitude of 10 mV, and the range of frequency was from 0.1 Hz to 100 kHz.

III. RESULT

The SEM images of the three kinds of fabricated iridium oxide samples are shown in Fig. 5. The SIROF shows a dendritic surface microstructure in Fig. 5(a), the AIROF in Fig. 5(b) shows a rough and porous iridium oxide layer, while the EIROF in Fig. 5(c) shows a loose microstructure with clear aggregation of tiny grains. The AIROF and EIROF show the similar microstructure because they usually obtain H_2O molecules in the film, which makes them more easily permeable for water and ionic species, resulting in a higher CSC. While the SIROF shows better stability due to its good adhesion to the substrate and the non-existent of H_2O molecule.

IV. DISCUSSION

Fig. 6 shows the CV and EIS of the three kinds of fabricated iridium oxide. After activation, the SIROF shows wide CV shape in Fig. 6(a). Meanwhile, there are no sharp peaks due to the high electrochemical activity of the redox reactions, which results in large pseudo capacitance and large CSC. The CSC of SIROF is 36.15 mC/cm^2, which is 5.7 times of the pre activation one. The detailed electrochemical performance data are shown in table 1. From 0.5 Hz -100 kHz, the impedance is significantly reduced (Fig. 6(b)) that the 1 kHz impedance after the activation is only 25.3% of the pre activation one. The SIROF is of more capacitance below 100 Hz and more resistance above 100 Hz after activation, which is shown in Fig. 6(c). The 1 kHz phase is -27 degree, nearly half of the pre activation one. Since the AIROF is transformed into the stoichiometric state during the activation process from iridium, the distinguished peaks in the CV curve are obtained shown in Fig. 6(d). After activation, the CSC of the AIROF microelectrode is 40.07 mC/cm^2, which is nearly 24 times more than that of iridium microelectrode. The impedance at 1 kHz of the AIROF microelectrode is 4064 ohm, about one-tenth of the pre activation one. In the whole frequency range, the impedance is substantially reduced shown in Fig. 6(e). The phase at 1 kHz of the AIROF microelectrode is -6.1 degree, about 8.6 % of the iridium microelectrode. Above 10 Hz, the AIROF is of more resistance and more capacitance below 10 Hz after activation, which is shown in Fig. 6(f). The CSC of as prepared EIROF (pre activation) is much larger than that of the SIROF and AIROF, which is 29.07 mC/cm^2. After activation, the CSC of the EIROF microelectrode is 68.20 mC/cm^2, which is the largest of the three kinds of iridium oxide. Although the EIROF is also the stoichiometric state as Ir(IV), the sharp peaks are disappeared compared to the AIROF shown in Fig. 6(g). The reason is that the loose microstructure of the EIROF obtains H_2O molecules in the grains. In the whole frequency range, the impedance is slightly reduced shown in Fig. 6(h). The impedance at 1 kHz of the

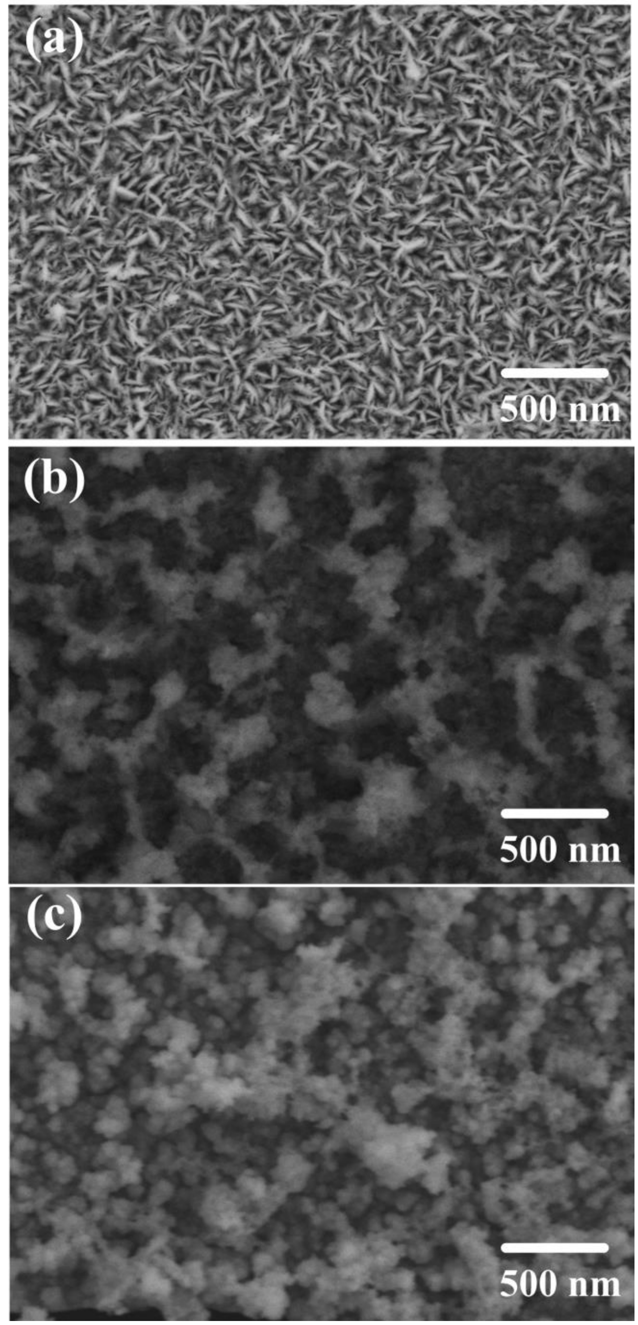

Figure 5. SEM images of the three kinds of fabricated iridium oxide samples. (a) SIROF, (b) AIROF, (c) EIROF.

TABLE I. ELECTROCHEMICAL PERFORMANCES COMPARISON OF SIROF-AIROF-EIROF MICROELECTRODES

Type	CSC (mC/cm^2)		1 kHz impedance (ohm)		1 kHz phase (- degree)	
	Pre activation	Post activation	Pre activation	Post activation	Pre activation	Post activation
SIROF	6.34	36.15	17300	4377	48.8	27.0
AIROF	1.69	40.07	41374	4064	70.7	6.1
EIROF	29.07	68.20	6936	3801	31.0	13.7

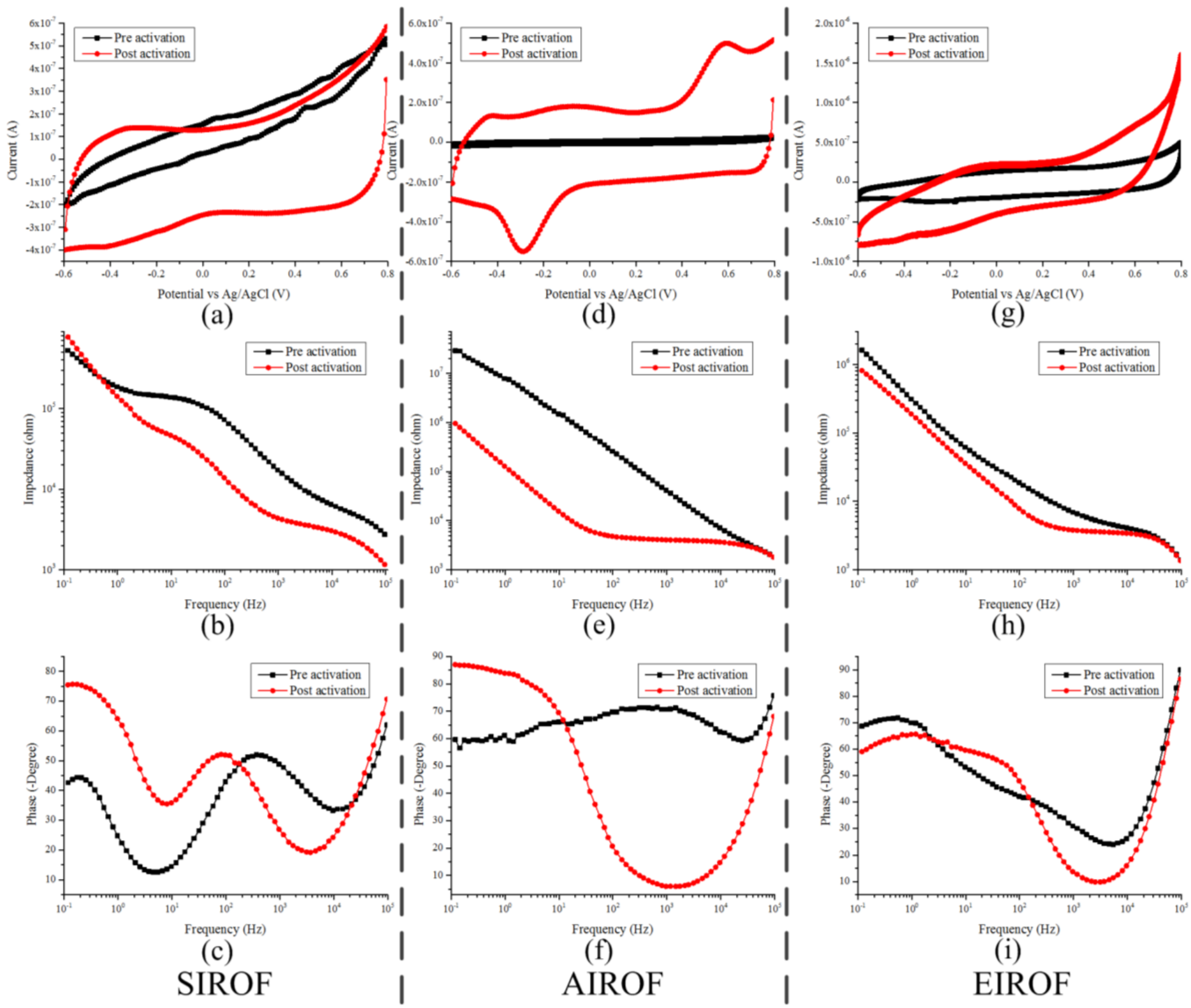

Figure 6. CV and EIS of three kinds of fabricated iridium oxide samples at pre and post activation states. (a-c) SIROF, (d-f) AIROF, (g-i) EIROF.

EIROF microelectrode is 3801 ohm, about one-half of the pre activation one. Above 150 Hz, the EIROF is of more resistance and more capacitance between 2-150 Hz after activation, which is shown in Fig. 6(i). The phase at 1 kHz of the EIROF microelectrode is -13.7 degree, about 44.2 % of the pre activation EIROF. Thus, it is suitable to use the EIROF for the short time electrical stimulation due to its largest CSC and lowest impedance. However, SIROF is more stable in the long time stimulation application owing to there is no water molecule. AIROF shows more potential application in the neural recording as a neural interface because of the most stable and lowest phase response.

REFERENCES

[1] K. Raeyoung and N. Yoonkey. Novel platinum black electroplating technique improving mechanical stability. *35th Annual Int IEEE EMBS Conference*, pages 184-187, 2013.

[2] B. Wessling, A. Besmehn, W. Mokwa and U. Schnakenberg. Reactively Sputtered Iridium Oxide: Influence of Plasma Excitation and Substrate Temperature on Morphology, Composition, and Electrochemical Characteristics. *J. Electrochem. Soc.*, 154:F83-F9, 2007.

[3] Y. Lu, Z. Cai, Y. Cao, H. Yang and Y.Y. Duan. Activated iridium oxide films fabricated by asymmetric pulses for electrical neural microstimulation and recording. Electrochem. Commun. 10:778-82, 2008.

[4] X. Kang, J. Liu, H. Tian, C. Zhang, B. Yang, Y. NuLi and C. Yang. Optimization and electrochemical characterization of RF-sputtered iridium oxide microelectrodes for electrical stimulation. *J. Micromech. Microeng.*, 24:025015, 2014.

[5] X. Kang, J. Liu, H. Tian, C. Zhang, B. Yang, Y. NuLi, H. Zhu, and C. Yang. Controlled activation of iridium film for AIROF microelectrodes. *Sens. Actuators B: Chem.*, 190:601-611, 2014.