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A Study of Nanoporous Platinum Electrode for EEG Signal Quality Enhancement

2015년 1월

서울대학교 대학원
협동과정 바이오엔지니어링 전공
김 도 윤
뇌파 신호 품질 향상을 위한 나노 다공성 전극에 대한 연구

지도교수 김희찬

이 논문을 공학석사 학위논문으로 제출함
2015년 1월

서울대학교 대학원
협동과정 바이오엔지니어링 전공
김도윤

김도윤의 공학석사 학위논문을 인준함
2015년 1월

위원장 최영빈 (인)
부위원장 김희찬 (인)
위원 이정찬 (인)
Abstract

The significance of biopotential recording has been increasing in both medical and non-medical fields. Accurate signal acquisition using minimally invasive and less cumbersome electrode is one of the key issues in the biopotential measurement. In this study, a new type of electrode, called L2-ePt electrode that utilizes the stable nanoporous platinum surface to reduce electrode-skin contact impedance is introduced. To determine the validity of using the L2-ePt electrode in biopotential recording applications, the L2-ePt electrode was compared to commercially available Ag/AgCl electrode and flat platinum electrode in terms of their electrode impedance levels both in solution and on human skin. Electroencephalogram signals on the subjects’ forehead were simultaneously acquired by each type of electrode to assess the signal correlation. In addition, steady-state visual evoked potential (SSVEP) responses were measured using commercially available gold-disc electrode, moistened-sponge L2-ePt electrode, and moistened-sponge flat platinum electrode for the signal-to-noise ratio (SNR) comparison. In the evaluation of the electrode-skin contact impedance and signal correlation, the L2-ePt electrodes performed significantly better than the flat platinum electrodes. Moreover, the paste-less L2-ePt electrode showed similar SNR performance to the commercial gold-disc electrode with paste. Therefore, the proposed L2-ePt electrode can be used even without paste to acquire accurate biosignals in applications where wet Ag/AgCl electrode is not suitable.

Keywords: Biopotential recording, nanoporous surface, platinum electrode, electrode impedance, electroencephalogram

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1. Introduction

1.1. Background

1.1.1. Biopotentials

Inside the human body, constant and complex physiological phenomena maintain our lives. Among many events occurring in the body, the ionic movement of excitable cells, such as neurons or muscle cells, is the fundamental working mechanism of the brain and muscular system (1, 2). Surrounding these cells, high concentration of chloride ions facilitates propagation of the ionic current. Since these ionic current flows create detectable potential differences at the surface of the body, for many years, researchers and clinicians have been using the electrical activity inside the human body, or biopotential, to monitor what is happening in our body (1, 3).

Because biopotentials are non-invasive, contain wealth of information about the internal condition of the body, and are relatively convenient to use, the use of biosignal has expanded beyond laboratory bench-tops and hospital care units to sports and entertainment (4). Thus, developing more accurate and convenient ways to measure biopotential has been one of the key topics of research for biopotential recording.

1.1.2. Electroencephalogram

An electroencephalogram, or EEG, detects and records brain electrical fields. EEG signals contain much of the brain’s information about wakefulness, perception, attention, and memory, just to name a few. Currently, the EEG is used not only for diagnosis in clinics, but also for consumer devices in daily life. For example, EEG recordings are used to diagnose epilepsy, evaluate the state of attention, mood, and many other cognitive conditions. Fur-
thermore, the EEG signals can be utilized in brain-computer interface application due to its non-invasiveness and high temporal resolution (5, 6).

1.1.3. Skin and Electrode Interface

To detect biopotentials at the body surface, electrodes convert the potential difference at the skin into electrical current to be processed by electronic devices (7). Because the electrodes change ionic current into electrical current, they are considered as electrical transducers (8). However, various factors must be considered for acquiring high quality signals from the surface of skin. In this section, some of the critical aspects are briefly introduced.

Skin

The structure of the surface that the electrode contacts is composed of various layers. The inner most layer is called the dermis, where vascular and nervous components reside. From the dermis, pain originates. The stratum germinativum is the layer above the dermis, and the cells in this layer divide and grow out toward the stratum corneum. Also, the stratum germinativum is electrically conductive. Right above the stratum germinativum, the stratum corneum is composed of dead cells and is responsible for protecting our body from harmful external environment. However, the stratum corneum is relatively non-conductive, thus acts as the major source of resistance to electrical current (1, 3, 9). The composition of the stratum corneum is as follows: 40 % large keratin (protein), 40 % water, and 20 % lipid (9). The stratum corneum allows coupling between the electrode and the conductive tissue beneath the stratum corneum. But, due to its varying thicknesses, ranging from 5 ~ 70 μm in different sites of the body, the capacitive value also varies and depends on humidity and the thickness of the layer (2, 10).

Skin preparation
In order to circumvent the electrically resistive stratum corneum, two common methods are employed. First, the skin is abraded to decrease the thickness of the stratum corneum to reduce the effect of the layer, and second, an electrolyte gel containing conductive ions, such as sodium or potassium, is applied to the skin to diffuse the ions into the stratum corneum to increase conductivity (1). Mild abrasion reduces the skin impedance by 100 to 1,000 fold (3). Furthermore, applying gel not only increases conductivity by ion diffusion into the stratum corneum, but it also increases the effective electrode surface area, further decreasing the impedance.

**Electrode-skin interface**

At the electrode-skin interface, charge arrangement induced by biopotential causes formation of the electrical double layer at the electrode-electrolyte surface (3). For wet electrodes, which uses conductive gel or paste in between the electrode and skin to create conductive pathway of ionic current, halfcell potential is created. By convention, a halfcell potential of a metal is a relative potential compared to that of the hydrogen electrode used as a reference(11). Halfcell potential can tell us the extent of the oxidation-reduction reactions occurring at the interface, and the charge distribution at the interface influences the performance of an electrode. Also, halfcell potential varies with the type of metal as well as electrolyte ions at the interface (12).

Here at the electrode-skin interface, another significant phenomenon called polarization takes place. Polarization occurs when faradaic current (i\textsubscript{DC}) flows through the electrode-electrolyte interface. This current flow disturbs the equilibrium which the interface was maintaining, and creates another voltage term by passing through a charge transfer resistance (R\textsubscript{ct}). A perfectly polarizable electrode has infinite value for charge transfer resistance, while a non-polarizable electrode has zero value for charge transfer resistance. Due to
polarization, varying potential drifts randomly with respect to the electrolyte (9). Thus, polarizability is one of the major source of noise from an electrode-electrolyte interface (1). Furthermore, a polarized electrode is capacitively coupled to the skin due to no net transfer of charge across the electrode-skin interface. On the other hand, a non-polarizable electrode that allows freely flowing charge across the interface is a resistively coupled electrode (12). Therefore, the charge transfer ability of an electrode determines whether an electrode is a capacitively coupled electrode or a wet electrode.

Other factors

In addition, various other factors, such as roughness of the interface surface and intra-human variations, influence the performance of an electrode. According to previous researches, an impedance of rough surface electrode is lower than that of a smooth surface electrode due to increased effective surface area of an electrode (8). Thus, large effective surface area can decrease the contact impedance of an electrode with a limited geometric surface area (3). Also, because of human to human differences in skin, it has been reported that the impedance of the skin varies with different individuals (8). Thus, when comparing different electrodes across individuals, the human variation must be taken into account.

1.1.4. Conventional Electrodes

There exist two main types of conventional biopotential recording electrode. One is a wet electrode that includes metal substrate and ionic gel surrounding the electrode. The second type, dry electrodes operate without the use of gel or paste. In this section, characteristics of the conventional electrodes, the Ag/AgCl electrode, dry/non-contact electrode, and microneedle electrode, are briefly introduced.
1. **Ag/AgCl electrode**

The Ag/AgCl electrode is the most universally used biopotential recording electrode for clinical applications due to its reliability and robustness. Because of its low charge transfer resistance, the Ag/AgCl electrode is weakly polarizing, making it stable against faradaic current (4, 9). Also, the gel placed in between the electrode and the skin make the stratum corneum to be ion conductive, which reduces the contribution of the skin in the impedance (2). Furthermore, the electrode adheres well to the skin and enables stable acquisition of signal with relatively low motion artifact (11).

Despite the advantages described above, the wet electrode possesses several undesirable drawbacks that limit its use. First, the long and frequent use of the electrode may be harmful for the users. It has been reported that the repeatedly using the electrode could cause allergic contact dermatitis. Secondly, the irritation of the skin may occur due to tearing of the outer protective layer of the skin from removal of the adhesive tape of the electrode. Also, repetitive application of gel with high concentration of ions could lead to allergic reaction for some of the subjects (10). Lastly, using the wet electrode on hair causes discomfort and inconvenience since the user has to wash after using the electrode. Thus, many researches have been conducted to make the use of electrode more comfortable and less damaging to the skin.

2. **Dry/non-contact electrode**

Dry electrodes use no electrolytic gel or paste to mediate the electrode and skin interface. Rather, these electrodes detect biosignals through capacitive coupling between an electrode metal and the skin (4). There are several advantages of using the dry electrodes than using the wet electrodes. First, using the dry electrodes is convenient for the users, since one does not have to apply paste and wash one’s body after the use. Secondly, the dry electrodes
are suitable for a long-term monitoring applications, since the electrodes do not cause the aforementioned damaging effects to the skin as the wet electrode does. Moreover, due to environmental moisture, such as sweat from our body, performance of the dry electrodes improve over time as the moisture at the electrode-skin interface increase coupling and effective electrode surface area (4). Thirdly, there is no real charge transfer between the body and the signal detection system, and therefore, the electrode are intrinsically safe (7). Thus, these electrodes are more suitable for users who have sensitive, damaged, or burned skin or for newborns (7).

However, the dry electrodes have high electrode impedance due to poor adherence to the skin. Also, this weak electrode-to-skin contact makes the electrode more prone to motion artifact (7). Therefore, using the dry electrodes on ambulatory patients and users who move freely might not be appropriate (2).

3. Invasive electrode

In addition to the wet and dry electrodes, microneedle type electrodes were developed to improve biosignal acquisition by bypassing the outer most skin layer. The stratum corneum has been one of the key reasons for using conductive gel in wet electrodes. The microneedle electrodes avoid the stratum corneum which contributes to the high electrode impedance, and the electrodes directly contact the stratum germinativum. Therefore, for the applications using the microneedle electrodes, neither skin preparation nor gel is necessary (1). However, due to the invasiveness of the microneedle electrodes, there is high risk of inflammation upon penetration. Also, after using the electrodes for a prolonged period of time, constant regeneration of the skin isolates the electrodes from the conductive body fluids. Therefore, the microneedle electrodes might not be effective for long-term use (2).
1.1.5. L2-ePt Electrode

In the present study, a novel dry nanoporous platinum electrode, or L2-ePt, is evaluated for its application as a biopotential recording electrode. Previously used in pH sensing or in glucose sensing, the L2-ePt electrode has been successfully fabricated using the electrodeposition technique described in earlier literatures. Here, descriptions of the fabrication principles and nanoporous electrode characteristics are presented.

1. Fabrication principle

The L2-ePt electrode is fabricated by mixing reverse micelle (L2) solution and platinum nanoparticles. Nanoparticles grow in aqueous regions of the micelles, which act as the template for nanoporous structure. After a controlled electrodeposition and removal of the L2 phases, a three-dimensional nanoporous platinum electrode called L2-ePt is created (13).

Figure 1. Fabrication principle of the L2-ePt electrode. Initially, a substrate metal is electrodeposited with solution mixed with L2 phases and platinum. Later when the L2 phases are removed from the electrodeposited surface, the nanoporous surface is constructed on the substrate metal.
2. Previous use

Due to nanoporous structures, the nanoporous structured electrodes have been used as solid state pH sensitive electrodes (14). Also, experimental results have shown that the nanoporous electrode enhances reduction of $O_2$, oxidation of glucose, and reduction/oxidation of $H_2O_2$ (15). Thus, the L2-ePt electrode has been investigated for various chemical reactions for its use as an electrochemical sensor.

However, the use of the nanoporous electrode had not been considered for biopotential recording applications. There are some properties of the electrode that make it a suitable candidate as a biopotential recording electrode. First, the electrode has high roughness factor, which is the ratio of effective surface area of an electrode to a geometric area (equation 1). Secondly, the fabrication of the L2-ePt is highly controllable and reproducible. The roughness factor of an electrode can be controlled by applying a constant voltage during the electrodeposition process (16). Furthermore, the electrode impedance decreases with enlarged roughness factor of a L2-ePt electrode. The surface of a L2-ePt is mechanically stable. Also, the electrode facilitates mass transfer of electrolyte through its nanopores, indicating the low pore resistance. In addition, the electrode exhibits high capacitance and low electrode impedance. Finally, platinum is biocompatible, thus it is safe to use for clinical therapies and even for neural prosthesis (15). Therefore, the nanoporous platinum electrode with low electrode impedance and high capacitance has been chosen to be used in biopotential recording application for the first time.

\[
Rf = \frac{\text{effective surface area}}{\text{geometric area}}
\]  
(1)
1.2. Objectives of Study

In this study, a new type of biopotential recording electrode is presented. The nanoporous platinum electrode utilizes the nanoporous character of the L2-ePt electrode to reduce the electrode impedance and then to enable high quality biopotential acquisition. To evaluate the validity of using the L2-ePt electrode in biopotential recording applications, the nanoporous platinum (L2-ePt) electrodes were compared to commercially available Ag/AgCl electrodes and flat platinum (FlatPt) electrodes. The electrode impedance analyses were conducted in solution to measure the contact impedance of each electrode. Then, the skin-electrode impedance was analyzed to assess the performance of the electrode on real human skins. Lastly, the L2-ePt electrodes were used to acquire electroencephalogram to compare the signal with that of the commercially available electrodes. The performance difference of each electrode in all experimental methods was statistically analyzed to observe significant differences between the nanoporous platinum electrode versus the other two electrodes. In addition, applicability of the L2-ePt electrode in EEG measurement over hair was observed by using moistened-sponge as a mediator between the scalp and the electrode. The signal-to-noise ratios of the L2-ePt and commercially available gold-disc electrode was compared to determine the usefulness of the new electrode in real EEG measurement situations.
2. Materials and Methods

2.1. L2ePt electrode Fabrication

2.1.1. Electrodeposition

**Instruments**

An electrochemical analyzer (Model CH660, CH Instruments Inc.) was used for bulk electrolysis (electrodeposition process) and cyclic voltammetry (electrode cleansing and surface area calculation) (Figure 2 and 3). During the cyclic voltammetry procedures, an Ag/AgCl (3 M KCl) electrode and a platinum wire were used as a reference and counter electrode, respectively. The active electrode was flat platinum foil during electrodeposition or nanoporous platinum electrodes during cyclic voltammetry.

**Electrodeposition and cyclic voltammetry**

According to previous researches done on the L2ePt electrode fabrication, nanoporous platinum layers were electrochemically deposited on platinum foil surfaces. Initially, a mixture of t-octylphenoxypolyethoxyethanol (Triton X-100; 50 wt %) (Sigma Aldrich), 0.3 M NaCl aqueous solution (45 wt %) (Sigma Aldrich), and hexachloroplatinic acid (HCPA; 5 wt %) (Sigma Aldrich) was made, and the mixture was heated up to 60 °C for through mixing. A platinum foil (Sigma Aldrich) was then inserted into the homogeneous mixture, and the electrochemical deposition process took place by applying a constant potential at -0.2 V versus Ag/AgCl (Figure 2). Here, the temperature was kept constant at 41°C using a water jacket connected to a thermostat. In order to remove the surfactant (Triton X-100) from the fabricated electrode surface, the electrode was placed under distilled water for 3~4 days, while the water was replaced every one hour.
Before measuring the surface area of the electrode, a cleansing process was carried out using cyclic voltammography. The electrode was placed in 1.0 M sulfuric acid solution and cycling potential was applied between +1.2 V and -0.22 V versus Ag/AgCl. The process was terminated when similar cyclic voltammograms were produced repeatedly.

The surface area of the electrode was determined from the hydrogen adsorption peaks of the cyclic voltammograms (scan rate 0.2 V s\(^{-1}\)) in 1.0 M sulfuric acid solution. As shown in equation (2), the conversion factor of 210 μC cm\(^{-2}\) was used to convert the unit from the cyclic voltammogram into cm\(^2\) (13).

\[
\text{Effective surface area} = \frac{\text{hydrogen adsorption area (μC)}}{210 \, \text{μC/cm}^2}
\] (2)

**Scanning electron microscopy**

To observe the nanoporous structure of the fabricated electrode, field emission scanning electron microscopy (FESEM) AURIGA39-37 (Carl Zeiss) was used.
Figure 2. Electrodeposition process of a L2-ePt electrode. First, electrode body is constructed using a flat platinum metal substrate. Then, the FlatPt electrode is electrodeposited through bulk electrolysis. After the electrodeposition, the electrode is submerged under distilled water to remove the surfactant. Finally, a L2-ePt electrode with its surface of electrodeposited nanoporous structure is produced.
Figure 3. Calculation process of roughness factor of an electrode from cyclic voltammetry. First, cyclic voltammetry is performed for a L2-ePt electrode or a FlatPt electrode. From the cyclic voltammogram, the hydrogen adsorption area is estimated. Then, the effective surface area of the electrode is calculated, which is then used in the roughness factor calculation.
2.2. Electrode Impedance Measurement

Electrical impedances were measured to analyze the impedance characteristics of the three different electrodes. As shown in Figure 4, a hollow and transparent acryl box (30 x 20 x 30 mm) with two circular holes (6 mm diameter) on two opposite sides was made. 0.9% NaCl solution (Daihan Pharmaceutical Company) was used as a medium between the two electrodes placed at the two opposing ends of the box. On one end of the box, a reference electrode (Ag/AgCl electrode; 3M) was placed, and on the other end, an electrode of interest, either Ag/AgCl, FlatPt, or L2-ePt electrode, was placed. Then, the electrodes were connected to an impedance analyzer 6440A (Wayne Kerr) for impedance measurements from 20 Hz to 1000 Hz (17).

Figure 4. A setup for electrode impedance measurement in 0.9 % saline solution.
2.3. Skin-electrode Impedance Measurement

The experiments were approved by the Institutional Review Board (IRB number H-1411-054-624). Skin-electrode impedance was measured using the three electrode method described by Spach et al. in 1966 (18). A total of eight subjects were tested for the skin-electrode impedance. Before measuring the impedance, skin preparation using skin prep gel (Weaver and Company), and the surface of the skin was checked and cleared of any small or visible particles. Then, the electrodes were cleansed with 83% ethanol (Samhyeon Pharmaceutical) before use.

Here, two reference electrodes and one active electrode was used to calculate the skin-electrode impedance on a right forearm (Figure 5). A function generator, AFG310 (SONY Tektronix), provided varying frequencies of 0.5, 1, 2, 5, 10, 20, 50, 100, and 200 Hz with constant voltage of 1 V. In order to make the experiment safe for the subject, current value less than 1 mA was necessary, and in this study, 100 μA was applied to the electrodes using 10,000 ohm resistor. The measured voltages between the I and II electrodes and II and III electrodes were then passed through instrumentation amplifier, INA 116, (Burr-Brown) for appropriate amplification of the signal. Electrode I and II were Ag/AgCl electrodes, and the electrode II was the active electrode, which was Ag/AgCl, FlatPt, or L2-ePt electrode. Finally, the output data was transferred to a computer using DAQ, NI-USB 6008 (National Instruments). Then the skin-electrode impedance (Z) was calculated by dividing the voltage measured between III and II electrodes (\(E_{II-III}\)) by the voltage measured between I and II electrodes (\(E_{II-I}\)), and the ratio was multiplied by the reference resistance (R) (equation 3) (18).

\[
Z = R \times \frac{E_{II-III}}{E_{II-I}}
\]  

(3)
Figure 5. A setup for skin-electrode impedance measurement. 
$R$=reference resistance (10,000 $\Omega$). $E_{II-III}$ represents the voltage between III electrode and II, and $E_{II-I}$ represents the voltage between II and I electrodes.
2.4. Electroencephalography

Electroencephalogram was obtained from four subjects, the forehead was prepared using the skin prep gel, and the electrodes were fixed in their stationary positions (Figure 6). The signals were acquired using three electrodes positioned as close as possible on forehead. In order to see dominant alpha waves (8 ~ 13 Hz), 20-second eye -closed and -open cycles were sequentially repeated for two minutes. The obtained data were band-pass filtered in MATLAB R2013a software (MathWorks) for three types of frequency bands. The first band, called ‘low band’, included 0.5 ~ 2 Hz, the second band, called ‘mid band’ included 5 ~ 20 Hz, and finally, the third band, called ‘high band’ included 50 ~ 200 Hz signals from the EEG recordings. Correlation coefficients were calculated between the Ag/AgCl electrodes and the FlatPt electrodes, and between the Ag/AgCl electrodes and the L2-ePt electrodes.

Figure 6. EEG recording setup on forehead (left) and eye-closed and –open cycles (right) during EEG measurement. The three electrodes are attached on the forehead of a subject as shown to measure the EEG signals from eye-closed and –open cycles for two minutes.
2.5. Steady-state visual evoked potential

Steady-state visual evoked potential (SSVEP) responses were measured from the occipital region of a participant (19, 20). In order to observe the effectiveness of moistened-sponge in measuring the brain activity, sponges used in Emotiv headset were installed onto the L2-ePt and FlatPt electrode surfaces. To moisten the sponge, 10–15 drops of contact lens solution was applied to the sponge. As for the visual stimulus, Psychophysics Toolbox extensions (Brainard, 1997; Pelli, 1997; Kleiner et al, 2007) was used to generate 10 Hz flickering image stimulus for 60 seconds on a LED monitor (Figure 7). For data collection, 8 subjects were tested with 3 trials per subject.

From the SSVEP response measurement, two sets of comparison were made to observe the performance of the L2-ePt electrode. The first set of comparison assessed simultaneous measurement of SSVEP responses from a moistened-sponge L2-ePt electrode versus a moistened-sponge FlatPt electrode. The second set of comparison observed simultaneous SSVEP responses for commercially available gold-disc electrode (Grasstechnologies) versus the moistened-sponge L2-ePt, and the moistened-sponge FlatPt electrode.

To observe the signal quality of different electrodes, SNRs were calculated for each electrode. The amplitude at 10 Hz stimulus frequency was used as the signal-power, while the noise-power was estimated by considering 95 percent of the ±1 Hz from the stimulus frequency of Fourier transform bins as noise (21).
Figure 7. An experimental setup for SSVEP response. A 10 Hz stimulus flickers for 60 seconds while a subject concentrates on the stimulus with the three electrodes attached to the occipital region of the head.
2.6. Statistical Analysis

For statistical analysis, SPSS IBM software was used. Here, one-way ANOVA was used to determine the significant difference between the three different electrodes. Then, Tukey post hoc test was used to observe the pairwise difference between the electrodes.

For the electrode impedance in solution experiment and the skin-electrode impedance experiment, one-way ANOVA and Tukey post hoc test were employed to compare the Ag/AgCl electrode, the FlatPt electrode, and the L2-ePt electrode. For the EEG analysis, independent t-test was used to assess the differences of the measured EEG signal correlations. Finally, for the SSVEP response experiment, one-way ANOVA and Tukey post hoc test were used to observe significant difference between the gold-disc electrode with paste, the L2-ePt electrode with moistened-sponge, and the FlatPt electrode with moistened-sponge.
3. Results

3.1. L2-ePt Electrode Fabrication

L2-ePt was electrochemically deposited on a platinum metal substrate. FESEM images were used to compare morphologies of the FlatPt electrodes and the L2-ePt electrodes. The comparison confirmed that the L2-ePt electrode had homogeneous nanoporous structures with ~10 nm pores, while the FlatPt electrode had distinguishable flat surface different from that of the L2-ePt electrodes (Figure 8A and B).

Figure 8. FESEM images of the electrodes
Morphologies of the FlatPt electrode (A) and the L2-ePt electrode (B). FESEM images are shown on the right (300,000 x magnification, scale bar=100 nm).
3.2. Roughness Factor Calculations

The definition of a roughness factor is the ratio of effective surface area to the geometric area of an electrode (15). In order to determine the roughness factors of the fabricated L2-ePt electrodes, cyclic voltammetry was performed using 1M H$_2$SO$_4$ solution with Ag/AgCl electrode and a platinum wire as a reference and a counter electrode, respectively. From a cyclic voltammogram, the hydrogen adsorption peak was integrated and converted with the conversion factor (210 $\mu$m cm$^{-2}$) to represent the area in cm$^2$. From the cyclic voltammograms of the FlatPt electrodes and the L2-ePt electrodes, it was evident that the L2-ePt electrodes had significantly larger area as observed in Figure 9A, meaning that hydrogen atoms attached to much larger surface area in the L2-ePt surfaces than on the FlatPt surfaces. To quantitatively determine the surface area of the fabricated electrodes, roughness factors were calculated. As shown in Figure 9B, a total of eight L2-ePt electrodes were fabricated with varying roughness factors (Rf<100, 200<Rf<300, and Rf>300) by applying constant voltage of -0.2 V, while varying the final charge value during the electrodeposition process. Although empirically determined, the final charge value of 0.5 C cm$^{-2}$ produced Rf of 100 electrodes, 1.0 C cm$^{-2}$ produced Rf between 200 and 300, and charge values higher than 1.5 C cm$^{-2}$ resulted in Rf greater than 300 (Figure 9B and C).
Figure 9. (A) Cyclic voltammogram of a FlatPt electrode (blue) and a L2-ePt electrode (red) showing enlarged surface area of the L2-ePt. The dotted circle indicates the hydrogen adsorption area. (B) Roughness factors controlled by the charges passed through during electrodeposition processes. (C) Average roughness factors of three different electrodeposition by charge.
3.3. Electrode Impedance Comparisons

The electrode impedances of the fabricated electrodes were analyzed by using an impedance analyzer under saline solution (0.9% NaCl solution). Figure 10 A shows the average electrode impedance of the three electrodes across the frequency range between 20 ~ 1,000 Hz. The result shows that the FlatPt electrodes had significantly high electrode impedance in frequency ranges from 20 ~300 Hz than those of the L2-ePt and the Ag/AgCl electrodes. It was also found that at 20 Hz, the average electrode impedance of the FlatPt electrodes was significantly different from those of the other two electrodes. On the other hand, the Ag/AgCl and the L2-ePt electrodes did not exhibit significant difference in average electrode impedance at 20 Hz (Figure 10B). Individual electrode impedances of the L2-ePt electrodes were also observed in the same frequency range as mentioned above. Although three roughness factors were controlled in the fabricated electrodes, it was revealed that there was no significant difference between the electrodes with roughness factors of 100, 200, and 300 throughout the frequency range as shown in Figure 11. Thus, the nanoporous platinum electrode had significantly low electrode impedance than the flat platinum electrode by nearly 100 fold. It was also notable that the L2-ePt electrodes exhibited similar level of electrode impedance as the Ag/AgCl electrodes throughout the entire frequency range.
Figure 10. (A) Impedance versus frequency graph of averaged data of the Ag/AgCl (empty triangle), FlatPt (empty diamond), and L2-ePt (filled circle) in solution from 20 ~ 1000 Hz. (B) Impedance comparison of the three electrodes at 20 Hz under solution. (* p<0.05)
Figure 11. Electrode impedance of L2-ePt electrodes with roughness factor less than 100 (triangle), between 200 and 300 (diamond), and larger than 300 (circle).
3.4. Skin-electrode Impedance Comparisons

Skin-electrode impedance was evaluated for eight individuals who participated in the present study. Figure 12 shows that the Ag/AgCl electrodes placed on different individuals exhibited considerable differences in their skin-electrode impedances. This deviation of the skin-electrode impedance in Ag/AgCl was identically observed in the same individuals for the measurements using both the FlatPt and the L2ePt electrodes. Calculated by dividing the skin-electrode impedance of an electrode of interest by the impedance of a Ag/AgCl electrode, the impedance ratios of the FlatPt and the L2-ePt electrodes were 10 ~ 20 times larger than that of the Ag/AgCl electrodes regardless of individual differences (Figure 13).

Furthermore, the skin-electrode impedances were compared in three frequency bands grouped by different EEG waves. From comparing the three electrodes in each band, it was found that the FlatPt electrode and the L2-ePt electrode were significantly different in the lowband and the midband (Figure 14 C and B, respectively). However, in the highband, the FlatPt electrode and the L2-ePt electrode did not show significant difference in their impedance ratios (Figure 14C).
Figure 12. Skin-electrode impedance data of Ag/AgCl electrode (A), FlatPt electrode (B), and L2-ePt electrode (C) (N=8).
Figure 13. Impedance ratio from each subject. Ag/AgCl (empty triangle), FlatPt (empty diamond), and L2-ePt electrode (filled circle) (Impedance ratio = $Z_{\text{skin-electrode of an electrode of interest}} / Z_{\text{skin-electrode of a AgAgCl electrode}}$).
Figure 14. Comparison of the electrode impedance ratios at lowband (A), midband (B), and highband (C). (* p<0.05)
3.5. Electroencephalogram Evaluations

The L2-ePt electrode was assessed for its performance in actual biopotential recordings. EEG from the forehead was measured from four subjects. From the eye-closed and -open cycles, it was expected to obtain strong alpha wave components during the eye-closed stages. The EEG measurements were bandpass filtered for 8~12 Hz frequency region. In the eye-closed sections of the data (Figure 15 A and B), correlation coefficients between the signals acquired by the Ag/AgCl electrodes and that of the FlatPt electrodes, and correlation coefficients between the signals obtained by the Ag/AgCl electrodes and that of the L2-ePt electrodes were compared. As shown in Figure 15 C, the mean correlation coefficient between Ag/AgCl and L2-ePt signals (r=0.91) and the mean correlation coefficient between Ag/AgCl and FlatPt signals (r=0.85) were significantly different (p<0.05) in the alpha wave region.
Figure 15. EEG signals acquired from Ag/AgCl electrode (red), FlatPt electrode (green), and L2ePt electrode (blue) during eye-closed stages (A and B). (B) is a merged image of the three signals. Mean correlation coefficients of Ag/AgCl vs. FlatPt and the mean correlation coefficient of Ag/AgCl vs. L2ePt (* p<0.05).
3.6. SSVEP Evaluation

The SSVEP responses were measured to estimate the SNR of the moistened-sponge L2-ePt electrodes, the moistened-sponge FlatPt electrodes, and the gold-disc electrodes with paste. The frequency spectrum confirmed the presence of a strong 10 Hz flickering stimulus (Figure 16A).

The moistened-sponge L2-ePt, moistened-sponge FlatPt, and paste using gold-disc electrodes were simultaneously used to record the SSVEP responses to the 10 Hz flickering visual stimulus. The conventional paste using gold-disc electrode, exhibited similar level of SNR as compared to that of the moistened-sponge L2-ePt electrode, while the moistened-sponge FlatPt electrode had significantly smaller SNR than those of the moistened-sponge L2-ePt and the gold-disc electrodes (Figure 16B and C). Consequently, the moistened-sponge L2-ePt electrode showed both high quality performance as well as convenience in the EEG recording application. The gold-disc electrode, even though the SNR was relatively steady, did not show significantly better SNR than that of the moistened-sponge L2-ePt electrode, which did not use paste.
Figure 16. SSVEP responses and SNR of the three electrodes. (A) shows the frequency spectrum of the SSVEP responses recorded from the gold-disc electrode with paste (red), the FlatPt electrode with moistened-sponge (green), and the L2-ePt electrode with moistened-sponge (blue) during 10 Hz flickering stimulus. Individual SNR results from the three electrodes and the combined SNR result from the SSVEP responses (B and C, respectively) (* p<0.05).
4. Discussion and Conclusion

4.1. Discussion

L2-ePt electrode fabrication

The L2-ePt electrodes fabricated in this work had similar morphological characteristics as reported in previous studies (13-16). The roughness factors were reproducibly controlled in electrodeposition processes, and the results suggest that the nanoporous electrodes used in this study were quantitatively controlled and fabricated.

Electrode impedance measurements in solution

Observations of the electrode impedance of the three electrodes suggest that the L2-ePt electrodes are capable of performing at a similar level as the commercially available Ag/AgCl electrodes. Due to the nanoporous surface, the large effective surface area of the L2-ePt electrodes reduces electrode impedance. More importantly, the surface area of the L2-ePt electrodes has noticeable influence on reducing electrode impedance in the presence of moisture. Meanwhile, the FlatPt electrodes had significantly large impedances.

Skin-electrode impedance measurements

This section of the study differs from that of the electrode impedance analysis under saline solution since there is no moisture mediating the skin and the electrode. By testing the electrode performance in practical situations, more realistic evaluation of the L2-ePt electrodes can made. As described by McAdams, individual skin varies greatly from person to person, and therefore the skin impedance also varies among different subjects (9). Likewise, individual differences in skin impedance were also observed in this study. Thus,
direct comparison across different individuals was difficult using the raw data of the skin-electrode impedance. However, it was observed that relative skin-electrode impedances of the FlatPt and the L2-ePt electrode to that of the Ag/AgCl electrode were constant throughout different subjects. Consequently, impedance ratios were used to compare different electrodes across the subjects.

To find meaningful relationship between skin-electrode impedance and EEG signals, the impedance ratios were compared in the three frequency bands defined in this study. The lowband from 0.5, 1.0, and 2.0 Hz included the delta wave of the EEG. The midband includes 5, 10, and 20 Hz frequency components, and the theta, alpha, and beta waves can be observed in this frequency region. Lastly, 50, 100, and 200 Hz region, or the highband, includes the gamma wave of the EEG. Therefore, from the evaluations of the three electrodes in three different bands, performances of the L2-ePt electrodes in each band can be related to the EEG recording situations.

**EEG measurements**

EEG measurements from forehead while closing eyes showed dominant alpha wave (8~13 Hz) component. In order to assess how accurately the L2-ePt electrodes detect the desired signal, the signals recorded from L2-ePt electrodes were compared to that of the ‘gold standard’ Ag/AgCl electrodes. Also, to observe the performance enhancement effect of the nanoporous surface, the same signals recorded from the L2-ePt electrodes were compared to that of the FlatPt electrodes. The significantly high correlation coefficient between the L2-ePt electrodes and the Ag/AgCl electrodes suggests that the L2-ePt electrodes perform with high reliability even compared to commercially available electrodes. Furthermore, significant enhancement in signal acquisition accuracy can be credited to the nanoporous surface of the L2-ePt elec-
trodes because the nanoporous platinum electrodes acquired better signals than the signals gathered by the FlatPt electrodes.

**SSVEP responses and SNR**

SSVEP responses of different electrodes showed that the L2-ePt electrode was optimal for measuring brain activities even over hair when moistened-sponge was used as a mediator between the hair and the electrode. The quality of the moistened-sponge L2-ePt electrode was similar or slightly better than that of the commercially available gold-disc electrode that uses paste. These outcomes suggest that the L2-ePt electrode can provide both convenience as well as performance for EEG recording applications, since the use of moistened-sponge does not require inconvenient use of paste as the conventional electrodes do.

**L2-ePt electrode in biopotential recording applications**

Therefore, the above assessments of the L2-ePt electrodes suggest that the nanoporous platinum electrode can perform with low electrode impedance and signal acquisition accuracy as the wet electrodes. Also, it is important to note that the L2-ePt electrodes can acquire high quality signal without using paste or gel as a medium. Thus, the L2-ePt electrodes can be employed in variety of application where using wet electrodes are cumbersome and inconvenient. Furthermore, the L2-ePt electrodes can perform with very low electrode impedance when used with moisture due to its nanoporous surface, as shown in the electrode impedance under solution experiment and the moistened-sponge experiment. Consequently, the L2-ePt electrode attached to the moistened sponge can be used for the EEG recordings over hair to provide both convenience and high signal quality acquisition capability. Therefore, the L2-ePt electrodes are suitable for a wide range of applications for its inde-
dependence from using paste while maintaining high quality signal acquisition performance. The characteristics of the L2-ePt electrode will be especially useful for the brain-computer interface applications where user comfort as well as excellent signal acquisition are important.

**Limitations**

Due to the limitation in electrodeposition technique, the only possible metal for the nanoporous surface structure was platinum. Biocompatibility and inert chemical property of the L2-ePt electrodes still make platinum metal desirable for long-term biopotential recording applications. However, there are various metals, such as aluminum, copper, and gold, which are used as biopotential recording electrode materials. Thus, an investigation on the effect of nanoporosity in different metals can suggest which metal is best suitable as a biopotential recording electrode in term of the signal quality and the cost.

**Future works**

For later studies involving biopotential acquisition applications, the nanoporous electrode can be incorporated with an active circuit to produce synergistic effect by simultaneously reducing the electrode impedance through the nanoporous electrode and enhancing the signal quality with the active circuit. Also, the use of the nanoporous electrode can be investigated in brain-machine interface applications, in which the electrode can provide more user friendly and practical solution than the wet electrode based systems.

4.2. Conclusion

From this study, the possibility and benefits of using nanoporous surface electrode as a biopotential recording electrode have been introduced. Using the nanoporous structure, the L2-ePt electrode was shown to outperform the
FlatPt electrodes. In the electrode impedance recording under solution, the nanoporous electrode had as low impedance as the commercially available Ag/AgCl electrodes. Furthermore, the skin-electrode impedance measurements revealed that the nanoporous electrodes were reliable and robust enough to repeatedly used and still maintain lower impedance than the FlatPt electrodes. Finally, for the EEG recording experiment, the L2-ePt electrodes performed with similar signal quality as the Ag/AgCl electrodes. In short, this study suggests that the nanoporous platinum electrode is a new method for biopotential recording in the future.
References

국문초록

뇌파 신호 품질 향상을 위한 나노 다공성 백금 전극에 대한 연구

김도윤
서울대학교 대학원
협동과정 바이오엔지니어링 전공

생체신호는 사람의 상태를 알려주는 중요한 지표 중 하나이다. 사람의 몸 내부에서 일어나는 현상을 외부에서 비침습적으로 관찰 한다는 점에서, 생체신호는 의료분야뿐만 아니라 엔터테인먼트 등 다양한 분야에 활용되고 있다. 유용한 정보를 제공해 주는 몸의 신호를 정확하고 편리하게 측정하기 위한 전극에 대한 연구는 꾸준히 진행되어 오고 있지만 각 전극은 각자의 한계점을 안고 있다. 본 연구의 목표는 나노다공성 구조의 백금 전극에 대한 연구를 통해 기존의 비 다공성 구조의 전극 보다
향상된 품질의 생체신호를 획득하는 것이다. 이를 위해, 첫째, 나노다공성 구조의 전극을 통제된 조건에서 제작하여 품질을 확인하고, 둘째, 생체신호 품질에 영향을 주는 전극 임피던스를 정량적으로 관찰하고, 셋째, 뇌파 측정을 통해 나노다공성 백금 전극과 기준이 되는 Ag/AgCl 전극과의 비교를 실행하였다. 그리고 마지막으로 정상 시각 유발 전위 (SSVEP) 반응을 물기를 머금은 스플즈를 사용한 백금 나노다공성 전극과 전도성 풀을 사용하는 디스크 금 전극과 비교 하여 착용자 편의성과 신호 품질에 관한 비교도 수행 하였다. 백금 나노다공성 전극을 생체신호 측정에 활용함으로써 생체신호를 보다 정확하고 편리한 방법으로 측정 하는데 유용하게 사용될 수 있을 것이다. 이전 백금뿐만 아니라 유사한 나노다공성 전극 표면을 가진 다른 물질을 사용하여 제작비용과 시간을 줄이면, 새로운 구조의 활용은 기존의 상용전극에서 찾을 수 있었던 단점을 보완 할 수 있어서 생체신호를 측정하는 사람뿐만 아니라 전극을 착용하는 사람에게도 도움을 줄 수 있을 것이다. 따라서, 본 연구에서 확인 할 수 있는 나노다공성 구조의 활용은 생체신호 측정에 새로운 접근 방식을 제시 할 것이다.

주요어: 생체신호 측정, 나노다공성 표면, 생체신호, 백금 전극, 전극 임피던스, 뇌파

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