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Development of A Flat Dry-pH-Sensor for Skin Surface pH Measurement

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Abstract. Recent reports suggest that skin barrier function and atopic dermatitis (AD) are related to the skin surface pH. The final aim of this study is to develop a multi-function skin measurement system for portable use, to evaluate data as pH, water content and etc. The system adopts a non-invasive measurement method of skin's surface pH without the use of any addition of water. In previous study, we reported about a Dry-pH-sensor that consists of a platinum wire electrode and Ag/AgCl wire electrode, based on the Nerstian response. Using the Dry-pH-sensor measurement system on the skin, we found that the voltage was constantly elevated. It is unclear whether elevated response may cause skin's water evaporation. We developed the Flat Dry-pH-sensor on the same basis of the previous one and realizing the sensor by adopting the ion-plating process. This paper describes the effects on the skin water content when measuring the skin surface pH with the Flat Dry-pH-sensor. The sensor was tested by using a standard pH solution. The correlation between pH-potential and voltage was found. All experiments were carried out on the left forearm of a male healthy subject, at room constant temperature and humidity (23℃, 30%RH). First, skin surface pH was measured for 2 min, then skin water content was measured for also 2 min; both measurements were executed in the same region of the forearm. Using the Flat Dry-pH-sensor resulted in the observation that with an elevated voltage value also the water content result was elevated, according to the time. Both the responses were analyzed by using the straight-line approximation. A negatively correlation between the sensor voltage and water content was found on the slope, also finding correlation on the intercept with the y axis. The response of the pH sensor voltage was influenced by the skin water content and the evaporation phenomenon was revealed.

Keywords: Skin surface pH, Flat Dry-pH-Sensor, Measurement, pH

1. Introduction

Human skin consists of three main tissues: the subcutaneous tissue, the dermis and the epidermis which contains the stratum corneum the outer part of the skin (Fig.1). Skin surface pH is measured on the epidermis's stratum corneum which includes different kinds of acids such as amino acids, lactic acid, fatty acid, etc. and includes numerous factors whose role well known as "acid mantel" function. The latter has been considered in terms of a defense mechanism against pathogenic microorganism and also having a main role in skin barrier homeostasis [1,2].

Measurements of skin surface pH and water content in the stratum corneum are useful in many non-invasive techniques used to objectively assess regarding atopic dermatitis and the skin barrier physical properties [3,4]. In addition, common loss-of-function genetic variants of epidermal barrier protein filaggrin are a major predisposing for atopic dermatitis [5]. They confirm that genetic variants of skin barrier protein influence the mechanism of atopic dermatitis, together with recent researches which also suggest that skin barrier function is related to the skin surface pH, which has role in the mechanisms generating atopic

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dermatitis [6,7]. Therefor the skin surface pH could be reflecting the skin barrier properties and it might be an important index to evaluate the skin condition and health. The final aim of this study is to develop a multi-function skin measurement system for portable use, to evaluate multi data as skin surface pH, water content, temperature and etc. The system adopts a non-invasive measurement method of skin's surface pH without the use of any addition of water. In a previous study, a Dry-pH-sensor consisting of a platinum wire electrode and Ag/AgCl wire electrode, based on the Nernstian response was reported [8]. Using the Dry-pH-sensor measurement system on the skin, we found that the voltage was constantly elevated. It is unclear whether elevated response may cause skin's water evaporation. We developed the Flat Dry-pH-sensor on the same basis of the previous one and realizing the sensor by adopting the ion-plating process. This paper describes the effects on the skin water content when measuring the skin surface pH with the Flat Dry-pH-sensor. First, the sensor's correlation between pH and potential response of voltage was tested using by pH standard buffer solution.

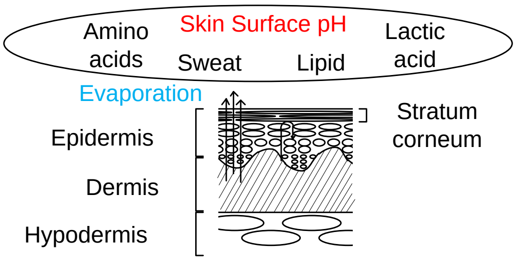

Fig.1: Skin structure with Skin surface pH and water evaporation

2. Material and Methods

2.1. Flat Dry-pH-Sensor

The sensor appearance is shown in Fig.2 (A). Electrodes are connected through copper tape respectively silver paste and lead. A schematic cross-sectional view of the sensor film layers is shown in Fig.2 (B). Base layers of titanium, platinum and silver were prepared by using the ion-plating process. Titanium layer is utilized for improving adhesion between the both layers with the substrate. Silver chloride layer was prepared by anodic polarization method. Reference electrode consists of silver, silver chloride and KCl; on the other hand the platinum surface works as working electrode according to the Nerunstian response. P-xylene, Nafion and KCl were prepared by chemical vacuum deposition. P-xylene works as selective membrane for protons. TPX (poly(4-methyl-1-pentene)) membranes, prepared by vacuum casting method.

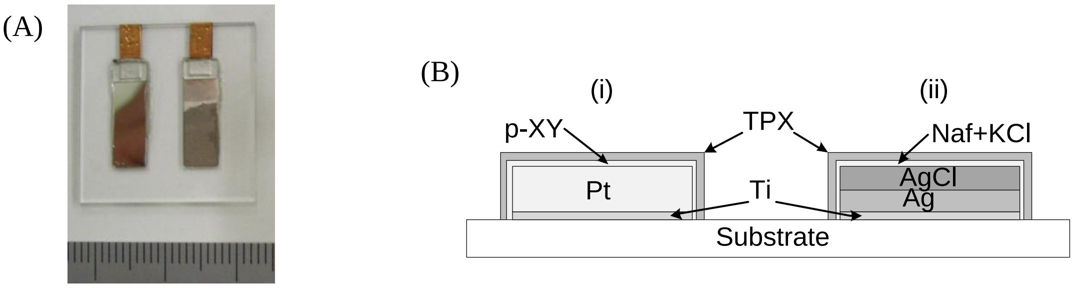

Fig.2: (A) Flat Dry-pH-Sensor: Substrate dimensions: 25 mm square×1.1 mm, Each electrode area: 5 mm × 10 mm (Approx.) (B) Schematic cross-sectional view of sensor film layers: (i) Working electrode, (ii) Reference electrode

2.2. Measurement

The measurements have been carried out with a DC microvolt ammeter (PM-18U, TOA Co. Ltd., Japan) with a personal computer equipped A/D interface with measurement program. Zero offset calibration have been done before measurements using two standard Ag/AgCl electrodes (RE-1B, BAS Inc., Japan) with 0.01 mol/l NaOH solution. As pH buffer solution was tested five types of solutions (pH 1.68, 4.01, 6.86, 9.18, 10.02) in contact to the sensor with a sampling sheet (Y011, Horiba Ltd., Japan). Sampling time is about 0.1 s and total time of measurement is 180 s for pH-potential response. All pH-potential response had been treated by moving average.

In Fig.3 (A), we reported the sensor potential response according to the time. The results indicate that too low and too high pH solution responses have a bit drifting. On the other hand middle pH responses were stable enough. It's clear that the observed phenomenon need more discussion. Relationship between pH-potential responses has been considered during 90 – 120 s time interval and the average of response has been reported with using straight-line approximation in Fig.3 (B). The reasons why we focused on the average values are that middle pH-potential responses were stable and because measurement procedure for skin was also of 120 s, as the measurement time in our study.

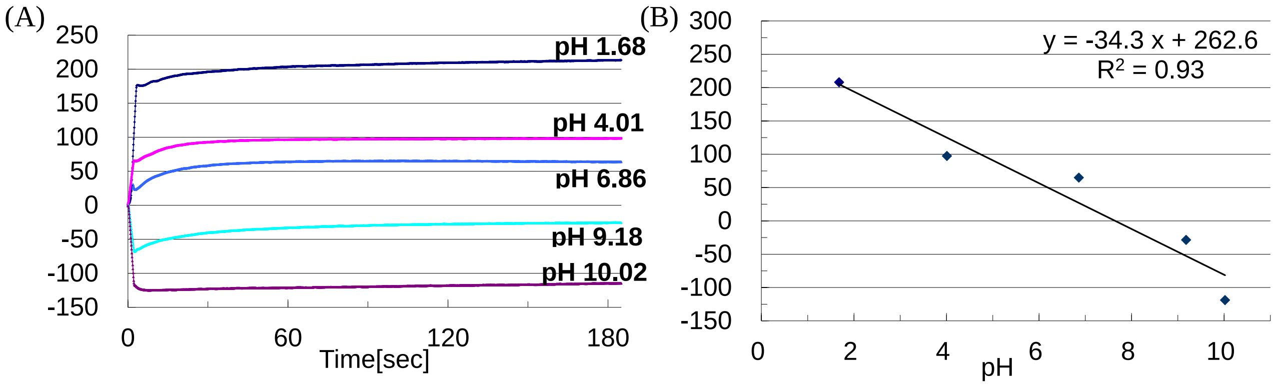

Fig.3: (A) Change of time related sensor potential response according to pH standard buffer solution.

(B) Relationship between pH-potential responses (Ave.90-120[sec]),

All measurements have been carried out on the left forearm of three male normal subjects in a room with constant temperature and humidity (23 ℃, 30% RH) and it were executed in the same region of the forearm. The subjects were requested to rest for about 15 minutes with exposure condition at forearm and with ground connection from their wrist to reduce any noise.

Skin surface pH measurements were performed for 2 minutes with 5 times without water added for having a non-invasive measurement. In our result we observed that response had some unstableness. Therefore, the responses results were all analyzed by straight-line approximation each 3-8 s, 30-120 s and 90-120 s. The selected condition was analyzed according to any part of these durations, R2 > 0.9 and Standard deviation < 2.5[mV]. Finally, one measurement response was selected each three subjects.

Skin water content was measured by a Corneometer (CM825, Courage + Khazaki Electronic GmbH, Germany). This instrument indicates the water content of human skin in arbitrary units. The method for measuring skin evaporation function by analyzing water content is the one of keeping the probe in contact with the skin during a 120 s measurement. The probe is coated by hydrophobic material therefore water evaporated from skin is collected on the surface of the sensor.

3. Results and Discussion

Fig.4 shows skin surface pH response measurement by using Flat dry-pH-sensor. The phenomenon of elevated response was shown by each subject.

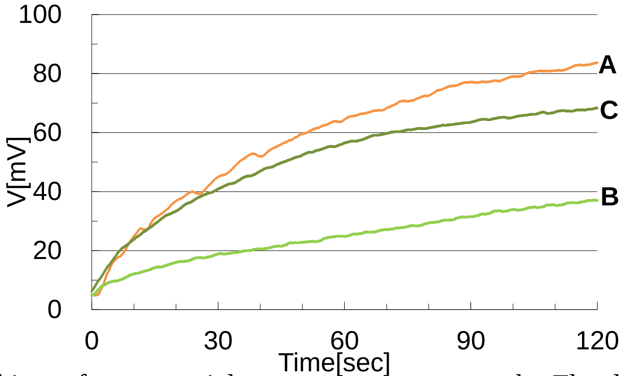

Fig.4: Skin surface potential response measurement by Flat dry-pH-sensor with non-invasive condition (Subject A, B, C)

This measurement was carried out with non-invasive condition as like the dry state. On the other hand pH-potential response tested in wet state. We have not yet investigated the results of potential response of skin surface to skin pH by Fig.3 (B) result. As can be seen from the results shown in Fig.3 comparing them to the ones of Fig.3 (A) the shapes and responses are different since the first part of responses are rising slowly and drifting all during measurement in skin.

Fig.5. shows the Skin water content measured for 120 s with probe had keeping contact with the skin during measurement made by Corneometer. The phenomenon of elevated response was moreover shown by each subject.

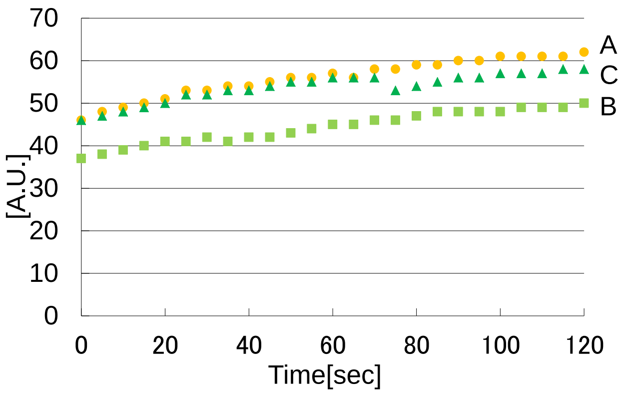

Fig.5: Skin water content with Corneometer probe keeping contact (Subject A, B, C).

Both of these results showed constantly elevated response observed which should be the affection of the skin's water evaporation especially in non-invasive measurement that is the no addition of water. The flat dry-pH-sensor measurements and Corneometer measurements were analyzed by using Straight-line approximation. The Straight-line approximation in the 90-120 s interval results of Fig.3 and Fig.4 of slope and intercept on the y axis are shown in Table 1.

Table 1 Skin surface pH and water content (by Corneometer) straight-line approximation of 90-120 s results. Slope and intercept on the y axis.

Subject	pH Sensor a[mV/t]	Corneometer a'[A.U./t]	pH Sensor b[mV]	Corneometer b'[A.U.]
A	0.238	0.057	55.08	54.86
B	0.178	0.064	15.88	41.96
C	0.148	0.071	50.62	49.50

Fig.6 (A) shows the slope correlation between flat dry-pH-sensor a[mV/t] and water content a'[A.U.] and there were found weak negatively correlation(R=0.76). Fig.6 (B) shows the intercept with the y axis between flat dry-pH-sensor b[mV] and water content b'[A.U.] and there were found strong correlation(R=0.95)

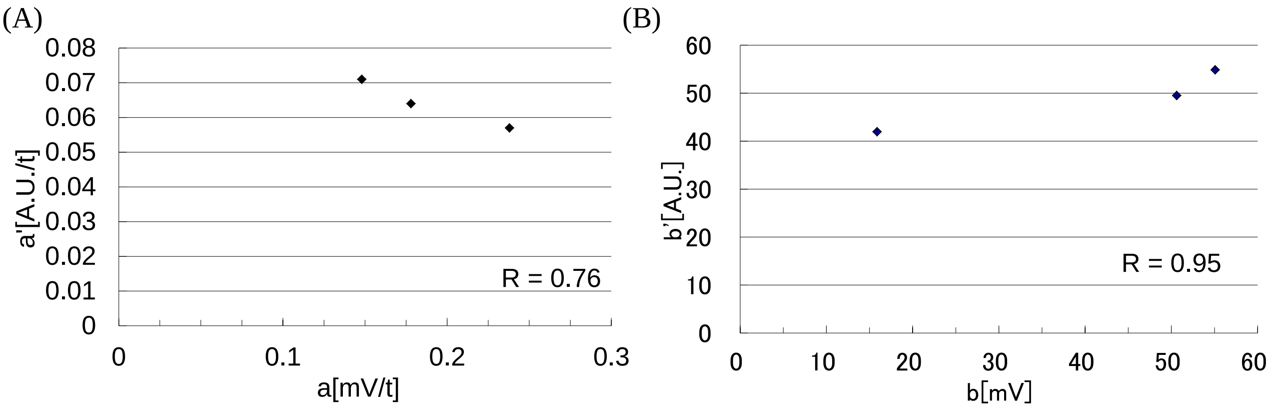

Fig.6: (A) Slope correlation between pH sensor a[mV/t] and water content a'[A.U./t]

(B) Intercept on the y axis correlation between pH sensor b[mV] and water content b'[A.U]

We believe that the Flat Dry-pH-sensor response on the skin is affected not only by the skin surface pH because of the constant elevated phenomenon which came under observation. There were not enough explanations for understanding which parts caused the skin surface pH response, which was affected by skin water content and also skin's water evaporation. Measurement of skin surface by using the pH sensor without added water, had slope and intercept on y axis mainly affected by skin's water content and evaporation was found from these results. Therefore, in the case of the pH sensor measurement with non-invasive method need cancel the effect of skin's water content and evaporation. We are considering about a formulating a mathematical model for constant elevated response according to skin's water content and evaporation and pH sensor measurement result should be corrected by using the model. Further studies are needed to confirm these methods of the model, model's parameters and which part has real meaning on skin surface pH of Flat Dry-pH-sensor measurements.

4. Conclusion

We developed a Flat Dry-pH-sensor for skin measurement based on a non-invasive method. Basic pH-potential response was fine with standard pH solutions. Using the Flat Dry-pH-sensor resulted in the observation of an elevated voltage value also together with an elevated water content result, according to the time. The both responses were analysed by using straight-line approximation. A negatively correlation between the sensor voltage and water content was found on the slope, also finding correlation on the intercept with the y axis. The response of the pH sensor voltage was influenced by the skin water content and the evaporation phenomenon was revealed. We are considering to use some model of water evaporation and filtering it to get real skin surface pH data.

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