Sensors and Actuators B 237 (2016) 49–53

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Totally shape-conformable electrode/hydrogel composite for on-skin electrophysiological measurements

Kuniaki Nagamine, Shun Chihara, Hiroyuki Kai, Hirokazu Kaji, Matsuhiko Nishizawa*

Department of Bioengineering and Robotics, Graduate School of Engineering, Tohoku University, 6-6-01 Aramaki, Aoba-ku, Sendai 980-8579, Japan

ARTICLE INFO

Article history:
Received 14 March 2016
Received in revised form 2 June 2016
Accepted 13 June 2016
Available online 15 June 2016

Keywords:
Electrode/hydrogel hybrid
Conducting polymer
Shape-conformable device
Electrophysiological measurements

ABSTRACT

An Au film electrode supported by a conductive elastic film was tightly bonded on a stretchable double-network hydrogel sheet by means of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) grown from the electrode surface into the hydrogel. This electrode/hydrogel composite showed stable resistance of $35 \pm 5\ \Omega\ sq^{-1}$ even during successive 20% stretching because of the pre-formed, designed cracks in the Au film. The large interfacial electric double layer capacitance ($9.5 \pm 0.3\ mF\ cm^{-2}$) of the PEDOT adhesive layer at the interface of the layered composite was found to stabilize the electrode potential against external noises, and decrease the electric impedance at the frequency of 5–500 Hz, which is the typical range of electromyographic signals. The electrical robustness and shape-conformability of the composite electrode were demonstrated by monitoring electromyographic signals of the joint of a human forefinger. In addition, it was also demonstrated that an ionic liquid-containing gel (ionogel) serves as a substrate of the composite for longer-term monitoring over 3 days on air-exposed human skin.

1. Introduction

Electrophysiological measurements such as electrocorticography, electrocardiography, and electromyography on the human body surface have been widely performed for medical diagnosis, medical monitoring, and neuron-to-machine interfaces for prostheses [1,2]. These electrophysiological measurement systems have recently been integrated into wearable devices for daily health monitoring and therefore, much effort has been paid for the development of flexible and stretchable electric devices [3–5] in order to ensure the motion adaptivity. For stable monitoring, it is necessary for electrode devices to maintain electric contact with the curvature of a skin even during body motion. Therefore, soft electrolyte gels are practically used as an interfacial material between the solid electrode devices and the soft skin. In fact, a commercially available Ag/AgCl patch is combined with an adhesive electrolyte gel [6]. While these conventional hydrogels are not elastic, stretchable hydrogels such as double network (DN) hydrogel have been recently developed [7,8]. By combining stretchable electrode devices and stretchable hydrogels, a totally shape-conformable electrode device could be realized for stable electrophysiological measurement at any parts of a body with motions.

In this study, we fabricated a shape-conformable electrode/hydrogel composite shown in Fig. 1, in which a stretchable Au electrode was tightly attached to the surface of a DN hydrogel sheet. The electrochemically deposited poly(3,4-ethylenedioxythiophene) (PEDOT) serves as a stable adhesive layer [9–11]. This PEDOT adhesive layer showed the advantage of low-impedance and low-noise measurement. In addition, it was also demonstrated that a non-volatile ionic liquid-containing gel (ionogel) can be used for longer-term monitoring of electrophysiological signals on skin.

2. Experimental

2.1. Fabrication of a double network hydrogel

The double network hydrogel was prepared according to the previously reported protocols [7]. The first prepolymer solution containing 1 M 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (NaAMPS, Sigma Aldrich) as a monomer, 40 mM N,N'-methylenebis(acrylamide) (MBAA, Wako Pure Chemicals) as a crosslinker, and 1 mM 2-oxoglutaric acid (Wako Pure Chemicals) as a photoinitiator was prepared. The solution was poured into the reaction chamber composed of two glass plates with a silicone

* Corresponding author.
E-mail address: nishizawa@biomems.mech.tohoku.ac.jp (M. Nishizawa).

http://dx.doi.org/10.1016/j.snb.2016.06.076
0925-4005/

spacer of 0.2 mm thickness between them. The reaction chamber was irradiated with UV light (365 nm, 8 W, Funakoshi) for 6 h in a nitrogen-filled glovebox. The obtained PNaAMPS hydrogel sheet was immersed in the second aqueous solution containing 3 M N,N-dimethylacrylamide (DMAAm, Sigma Aldrich), 3 mM MBAA, and 1 mM 2-oxoglutaric acid for 2 days at room temperature in the dark. The hydrogel sheet was again irradiated with UV light for 6 h in the nitrogen-filled glovebox to polymerize the second hydrogel, followed by washing with distilled water overnight to remove residual cytotoxic monomers. The resulting DN hydrogel has a thickness of about 0.5 mm after swelling in PBS solution.

2.2. Fabrication and evaluation of electrode/hydrogel composite

The Au arrays of 0.2 mm × 0.2 mm square tiles with 5 μm gaps were prepared by photolithographic patterning of sputtered Au (425.6 ± 20.6 nm (n = 3) thickness) on a glass substrate [12]. A composite film of PEDOT and polyurethane (PEDOT/PU) was prepared on the Au arrays as described in our previous report [9], by spin coating (750 rpm, 30 s) of a precursor solution and its thermal polymerization at 100 °C for 10 min. The precursor solution used here was a mixture of butanol (2 mL, Wako Pure Chemicals), EDOT (0.88 mL of 1 M solution, Clevios MV2, Heraeus), pTSFe(III) (6.5 mL of 0.4 M solution, Clevios C-B40V2, Heraeus) and 10 wt% PU/tetrahydrofuran solution (35 mL, Gumthane AR650, a kind gift from Okada Engineering Company). The thickness of the PEDOT/PU film, measured by a probe type step profiler (DEKTAC150), was approximately 3 μm. The Au-PEDOT/PU film on the glass plate was immersed in distilled water overnight to remove residual cytotoxic monomer and dopant, and cut out to a desired pattern by a cutting plotter (Craft ROBO Pro, Graphtec). A DN hydrogel sheet (0.5 mm thick) was then placed on the patterned Au-PEDOT/PU film. After permeation of monomer solution (50 mM EDOT and 100 mM $LiClO_4$ aqueous solution) into the hydrogel sheet, PEDOT was electropolymerized (300 mC cm^{-2}) to anchor the electrode to the hydrogel film [9–11]. Finally, the resulting electrode/hydrogel composite film was gently peeled from the glass substrate and further immersed in water overnight to remove residual EDOT monomer.

For the resistance measurement during stretching, four-point probes were attached at the two ends of the Au-PEDOT/PU film (10 mm width and 30 mm length), which was elongated at a strain rate of 0.1 mm s^{-1} using an electrically driven stage (SGSP O-35, Sigma Koki). A constant current of 10 mA was applied to the two outer probes using a Keithley 2400 SourceMeter and the potential difference was measured using the two inner probes connected to a voltmeter (ALS760C, BAS Inc., operated in the voltmeter mode) during stretching.

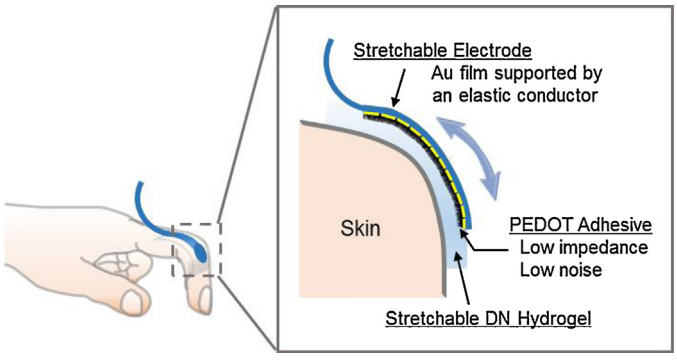

Fig. 1. Schematic illustration of the developed shape-conformable electrode/hydrogel layered composite on a forefinger.

2.3. Interfacial AC impedance measurement and cyclic voltammetry

AC impedance at the interface between electrodes and DN hydrogels hydrated with PBS solution was measured in a three-electrode configuration using an electrochemical analyser (ALS760C, BAS Inc., operated in the AC impedance measurement mode). A Pt flag (counter electrode) and Ag/AgCl (reference electrode) were placed in contact with the surface of the DN hydrogel to ensure ionic connection and the AC impedance was measured by applying 5 mV_{p-p} voltage at 1 Hz–100 kHz.

AC impedance on skin was measured by placing the electrodes on a human subject. Commercially available, adhesive gel-assisted Ag/AgCl electrodes (NM-31, Nihon Koden) were used as counter and reference electrodes. For the measurement on a forearm, the working (tested) and counter electrodes were placed on the forearm 5 cm away from each other, and the reference electrode was placed on the arm 30 cm away from the working electrode. For the measurements on a forefinger joint, the working electrode was placed on the joint of a forefinger, the reference electrode 5 cm away from the working electrode, and the counter electrode on a wrist.

Cyclic voltammetry was performed in the same three-electrode configuration setup using a potentiostat (ALS760C, BAS Inc., operated in the cyclic voltammetry mode). The potential applied to the working electrode was cycled between −0.4–0.4 V vs. Ag/AgCl at a scan rate of 10 mV s^{-1} while the current was measured.

2.4. Evaluation of the potential stability

The potential difference between the test electrode and the reference Ag/AgCl electrode was measured using a voltmeter (ALS760C, BAS Inc., operated in the voltmeter mode). The test electrodes were a bare Au film covered by a DN hydrogel hydrated with PBS solution and the Au-PEDOT/PU electrode/DN hydrogel composite with the entangling PEDOT adhesive. The reference Ag/AgCl electrode was placed in contact with the surface of the DN hydrogel to ensure ionic connection. A Keithley 2400 SourceMeter was connected to the circuit in series to inject ± 1 nA of constant current as a model of external noise. After waiting for 30 s, a constant current of +1 nA was applied on the test electrode for 30 s, then the current was turned off for 30 s, followed by a current of −1 nA for 30 s during the recording of the potential difference.

2.5. Electromyographic (EMG) signal measurements

EMG signal measurement was performed by placing the Au-PEDOT/PU electrode/DN hydrogel composite on the joint of a forefinger to ensure the contact between the hydrogel surface and the skin, and the gel-assisted Ag/AgCl electrode on the back of a subject's hand 5 cm away from the composite. Another gel-assisted Ag/AgCl electrode was placed on the wrist as a ground electrode. These electrodes were connected to the wireless EMG logger (input impedance: 10 TΩ, SPORTS SENSING Co., LTD) to detect EMG signals during repeated bending motion of the joint of a forefinger.

3. Results and discussion

The stretchable conductors are the key component of the present electrophysiological sensing device. We employed an Au film supported by an elastic conductor that is the composite of conducting polymer PEDOT and polyurethane (PU) [9], which is noted as Au-PEDOT/PU electrode in this manuscript. The attachment of Au on the PEDOT/PU was strong enough as checked by a scotch tape test. At first, we tried to use a continuous Au film. However, the resistance of this Au-PEDOT/PU electrode randomly