## Supporting Information

# Porous Microneedle-Based Potentiometric Sensor for Intradermal Electrolyte Monitoring 

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## Materials and fabrication of MN chip containing porogen

A monomer stock solution consisting of a glycidyl methacrylate ( 10 mL , FUJIFILM Wako Pure Chemical Corporation, Ltd.), trimethylolpropane trimethacrylate ( 5.23 mL , Sigma-Aldrich Co.) and triethylene glycol dimethacrylate ( 15.7 mL , FUJIFILM Wako Pure Chemical Corporation, Ltd.) was prepared at $25^{\circ} \mathrm{C}$. A porogen stock solution consisting of a mixture of polyethylene glycol $(4.0 \mathrm{~g}$, FUJIFILM Wako Pure Chemical Corporation, Ltd.) and diethylene glycol monomethyl ether ( 20 mL , FUJIFILM Wako Pure Chemical Corporation, Ltd.) was prepared at $65^{\circ} \mathrm{C}$. The monomer and porogen stock solutions were mixed (11:9 in volume) at $40^{\circ} \mathrm{C}$ with the addition of a photoinitiator (Irgacure 184; FUJIFILM Wako Pure Chemical Corporation, Ltd.). The precursor solution was poured into the female polydimethylsiloxane (PDMS) (SILPOT 184; Dow Corning Toray Co., Ltd.) mold, and degassing was performed under a vacuum of -0.096 MPa for 80 min to completely fill the microneedle-shaped cavities of the mold with the prepared solution. Photopolymerization under irradiation with 365 nm UV light (Model UVL-28; Funakoshi Co., Ltd.) was conducted for 3 h at $25^{\circ} \mathrm{C}$ under a nitrogen atmosphere.


Fig. S1. Plots of potential differences of Pt electrodes with different numbers of $\mathrm{Na}^{+}$ISM solution applications ( $\mathrm{n}=3$ independent experiments; mean $\pm$ SEM). For comparison, the potential difference at 5 mM is defined as 0 mV .

## Biocompatibility evaluation of ion-selective PMN electrode

The $\mathrm{Na}^{+}$ISM/PMN electrode was sterilized using an autoclave and soaked in the medium for 24 h (Fig. S2a). Normal adult human dermal fibroblasts ( $3.8 \times 10^{4}$ cells $/ \mathrm{cm}^{2}$, NHDF-Ad, Lonza) were seeded to a 48 -well dish and cultured for 24 h at $37^{\circ} \mathrm{C}$ and $5 \% \mathrm{CO}_{2}$, and subsequently, the supernatant was replaced with the medium soaked with the electrode (medium (+)). After three days of cell culture, the wells containing cells were washed twice with PBS, followed by treatment with the LIVE/DEAD ${ }^{\text {TM }}$ Viability/Cytotoxicity Kit (Thermo Fisher Scientific). The fluorescence images were randomly captured using a fluorescence microscope for each well (Fig. S2b), and image analysis was performed using ImageJ software to determine the percentage of live/dead cells in each sample. As shown in Fig. S2c, the viability of the cells is as high as that of the control sample (medium (-)), which was cultured with a medium without presoaking the electrode.


Fig. S2. (a) Schematic of normal adult human dermal fibroblasts (NHDF-Ad) seeded to a 48-well dish and cultured for 3 days in cell culture medium. (b) Live/dead staining of the cells cultured with the medium with $(+)$ and without ( - ) presoaking the ion-selective PMN electrode for 24 h . (c) Cell viability derived from image analysis for the cases with $(+)$ and without $(-)$ presoaking the ionselective PMN electrode ( $\mathrm{n}=3$ independent experiments; mean $\pm$ SEM).


Fig. S3. (a) Potentiometric response and (b) calibration curve of the $\mathrm{Na}^{+}$ISM/PMN electrode to the NaCl solution after measurements using pig skin ( $\mathrm{n}=3$ experiments; mean $\pm$ SEM).

