INTEGRATED HYDROGEL-POROUS SILICON STRUCTURES FOR NON-INVASIVE BIOSENSING

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I. Introduction

Hydrogels are water-infused, biodegradable polymer networks. They make cheap and environmentally friendly materials that interface well with human skin. Alginate hydrogels are particularly useful because of their uniquely malleable yet supportive structure. These characteristics make them an ideal medium for supporting mesoporous Silicon membranes and simultaneously assimilating into a wide range of tissues. **(Figure 1)**

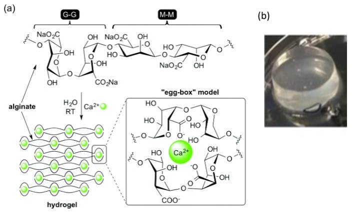


Figure 1. (a) Structure of alginate, composed of (1 → 4)-β-D-mannuronic acid (M) and (1 → 4)-α-L-guluronic acid (G). Hydrogels form an "egg-box" like structure through coulombic interactions with Ca^{2+} ions in solution.[1] ; b) Slow gelling alginate hydrogel [2]

Porous silicon (pSi) is utilized to measure and conduct electrical signals throughout the hydrogel. pSi membranes exhibit measurable current values as a function of voltage, which we will use to detect bioelectrical stimuli such as the concentration of physiologically relevant ion species such as sodium, potassium, and calcium.

II. Materials and Methods

A. Mesoporous Silicon Etching Process

Porous Silicon membranes ~110 μm thick and 79% porosity are fabricated from the anodization of low resistivity (100) Si in methanolic HF at an applied bias of 100 mA/cm^2 for 30 min.

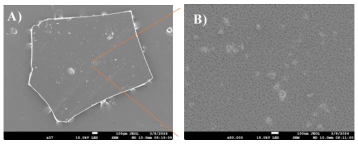


Figure 2. Scanning Electron Microscopy (SEM) images of a Mesoporous Silicon membrane (courtesy of Will Burnett, (TCU Chemistry):
(A, scale bar 100 μm)
(B, scale bar 100 nm)

B. Porous Silicon Diode Fabrication

- Cu electrode (0.25mm d) is attached to a pSi membrane (4 mm^2) via Ag-Epoxy
- Heated for 10 minutes @150℃
- Cooled for 10 minutes
- Ag epoxy is coated with thin layer of acetate nail polish

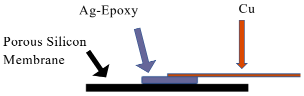


Figure 3. pSi Diode

C. Alginate Hydrogel Mixture Procedure and Hydration

The following ingredients are transferred into a microplate well:

- 2% w/v alginate (800 μL in each well)
- 0.36 M $CaCl_2$ (200 μL in each well)
- 0.34 M Glucono delta-lactone (200 μL in each well)
- Seal and incubate in humidity chamber in a 24 well microplate for 4 days for optimal viscosity

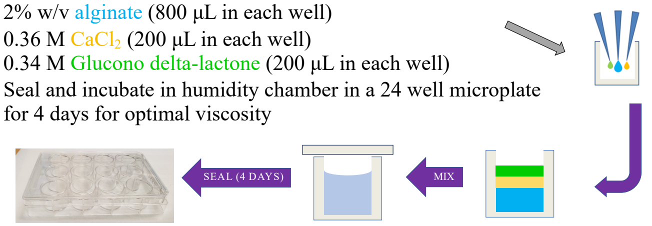


Figure 4. Hydrogel fabrication process in Microplate wells

D. Electrochemical Cell Fabrication

- Two pSi membranes are positioned parallel to each other, 2-3 mm apart.
- Diodes are attached to a glass slide set up, placed over microplate well acting as aqueous ion / hydrogel-containing electrochemical cell.
- Current-voltage measurements are obtained using a Keithley 2420 Sourcemeter.

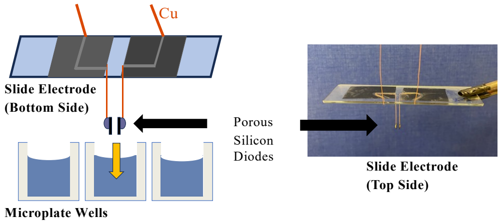


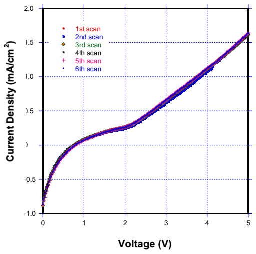
Figure 5. pSi diode configuration on glass slide

III. Results

Experiments center around integrating porous silicon membranes into aqueous environments and hydrogels to test how variations in ion concentration affect the current flow as a function of applied voltage. In each experiment, an electrochemical cell is created by placing two porous silicon membranes parallel each other 2-3 mm apart in solution/hydrogel. Current is recorded as a voltage bias is applied from zero to five volts four times per trial.

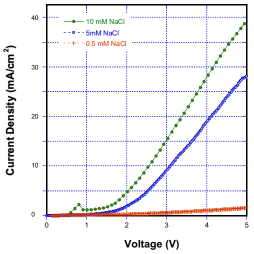
A. Initial Stability Tests : Current/Voltage Measurements (pSi diode + 0.5 mM NaCl)

- Classic Schottky behavior is observed
- After initial burn-in sweep, current response to applied voltage is very stable.



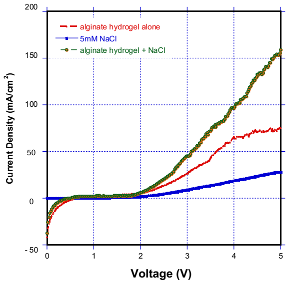
B. Current/Voltage Response of pSi Membrane to [NaCl]

- Magnitude of maximum current response is proportional to ion concentration present in the electrolyte (in the range 0-10 mM NaCl).



C. Current/Voltage Response to Immersion in Alginate Hydrogel

- A 100x amplification of measured current upon immersion of the electrolyte species in the alginate matrix (analogous to std addn).
- Addition of 20 μL of concentrated (1M) NaCl solution to a ~1 cm thick hydrogel/pSi cell results a doubling of measured current.



IV. Conclusions

- We have successfully demonstrated the ability of porous Si in membrane form to serve as concentration-dependent sensors for the evaluation of simple physiologically relevant ions such as sodium.
- The electrochemical response of such diodes in aqueous salt solutions is both stable and reproducible.
- Switching to an alginate hydrogel environment results in a rather significant enhancement in current response at a given voltage and sodium concentration.

V. Future Work

- Evaluate the actual ion concentrations (via EDX or the equivalent) present in a given pSi diode after use.
- Miniaturization of the pSi/Hydrogel sensing platform for compact applications.
- Methods for providing ion selectivity to the pSi diode.

VII. References

1. V. Alegre-Requena, Juan, et al. "Regulatory Parameters of Self-Healing Alginate Hydrogel Networks Prepared via Mussel-Inspired Dynamic Chemistry." *New Journal of Chemistry*, Royal Society of Chemistry, 3 Aug. 2016.
2. Growney Kalaf,, Emily A. ; Flores, Reynaldo ; Bledsoe, J. Gary ; Sell, Scott A." Characterization of slow-gelling alginate hydrogels for intervertebral disc tissue-engineering applications," Materials Science and Engineering: C, 2016, 63, 198-210.
3. Canham, Leigh. "Porous Silicon Formation by Anodization." *Handbook of Porous Silicon*, Springer International Publishing, Cham, Switzerland, UK, 2018.

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