Voltammetric pH sensing with 3D-printed graphene/poly(lactic acid) electrodes

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Introduction

- Monitoring astronaut health over long-duration space missions is a major challenge
  - Long travel times
  - Limited mass/power demands
  - Unexpected challenges
- 3D-printing is a technology that allows us to make customizable electrochemical sensing and energy storage devices *in silico*[1]
- We can develop devices on earth and then fabricate them at the point of use[2]
- Here, we developed voltammetric 3D-printed sensors for monitoring pH in complex biological fluids and consumables[3]

Methods

- Fabricated 3D printed electrode using graphene/PLA filament epoxied in a pipette tip
- Performed 3 step pretreatment on electrode
- Collected pH measurements in carmody buffers using square wave voltammetry (SWV)

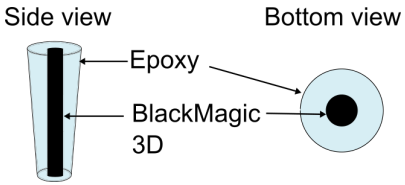

Figure 1: Schematic of 3D printed electrode

Activating Functional Groups

- We used four electrochemical pre-treatments to activate surfaces for voltammetric pH-sensing
  1. Polished electrodes using alumina slurries
  2. Applied +1.4 and -1.0 V in 0.5 M NaOH
  3. Polarized galvanostatically in 2 M H_2SO_4 and 1 M KNO_3
  4. Conditioned 1000 SWV cycles in a 4 pH buffer

pH calibration in buffer

- The peaks in SWV are indicative of redox processes or concentration of active species
- A linear plot was derived by performing SWV on buffers ranging from 3.97 to 8.83 pH (figure 4)

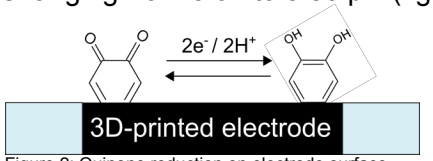

Figure 2: Quinone reduction on electrode surface

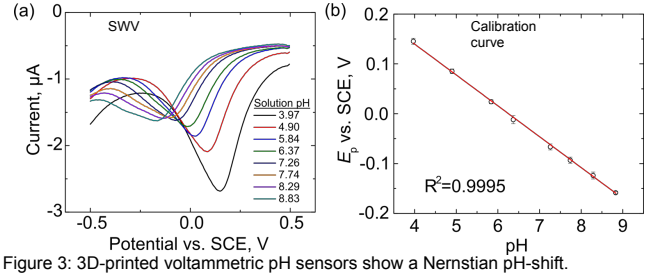

Figure 3: 3D-printed voltammetric pH sensors show a Nernstian pH-shift.

pH measurements in complex samples

- Applicability was tested by performing SWV in undiluted complex samples
  - Clear and well-defined peaks were observed

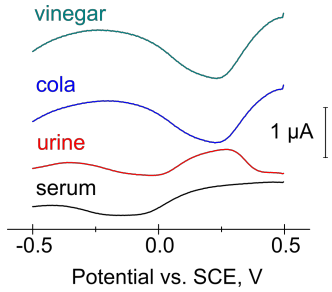

Figure 4: SWV traces of 3D printed sensor in real samples

- The sensor was compared to a commercial glass electrode
  - Strong reproducibility and accuracy

Table 1: Comparison of commercial glass pH electrode and 3D printed electrode

Sample	pH (glass)	pH (blackmagic)	% error
Vinegar	2.47(±0.04)	2.52(±0.07)	2
Soda	2.51(±0.10)	2.56(±0.08)	1.8
Urine	6.65(±0.02)	6.44(±0.04)	3.2
Horse Serum	7.26(±0.04)	7.56(±0.09)	4.1

Acknowledgements

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References

[1] G.D. O'Neil, S. Ahmed, K. Halloran, J.N. Janusz, A. Rodríguez, I.M. Terrero Rodríguez, *Electrochem. Comm.* **2019**, *99*, 56-60.
[2] G.D. O'Neil, *Curr. Opin. Electrochem.* **2020**, *20*, 60-65.
[3] F. Rabboh, G.D. O'Neil, *in prep.*