Simple Method for Preparing Customizable Pyrolyzed Photoresin Carbon Electrodes Using 3D Printing

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Introduction

Pyrolyzed photoresist electrodes (PPEs) are traditionally fabricated in a cleanroom using photolithography. Here, we present results demonstrating a simple and accessible fabrication method using stereolithography (SLA) 3D printing to prepare customizable pyrolyzed carbon electrodes. Stereolithography is a type of 3D printing that hardens a liquid resin after exposure to UV light, thus facilitating the production of small features. Following pyrolysis, the carbon electrodes prepared using 3D printing exhibited electrochemical behavior consistent with glassy carbon, thus showing their applicability for electrochemical analysis.

Figure 1. Three different custom electrodes 3D printed and pyrolyzed using this method.

Dimensional Measurements

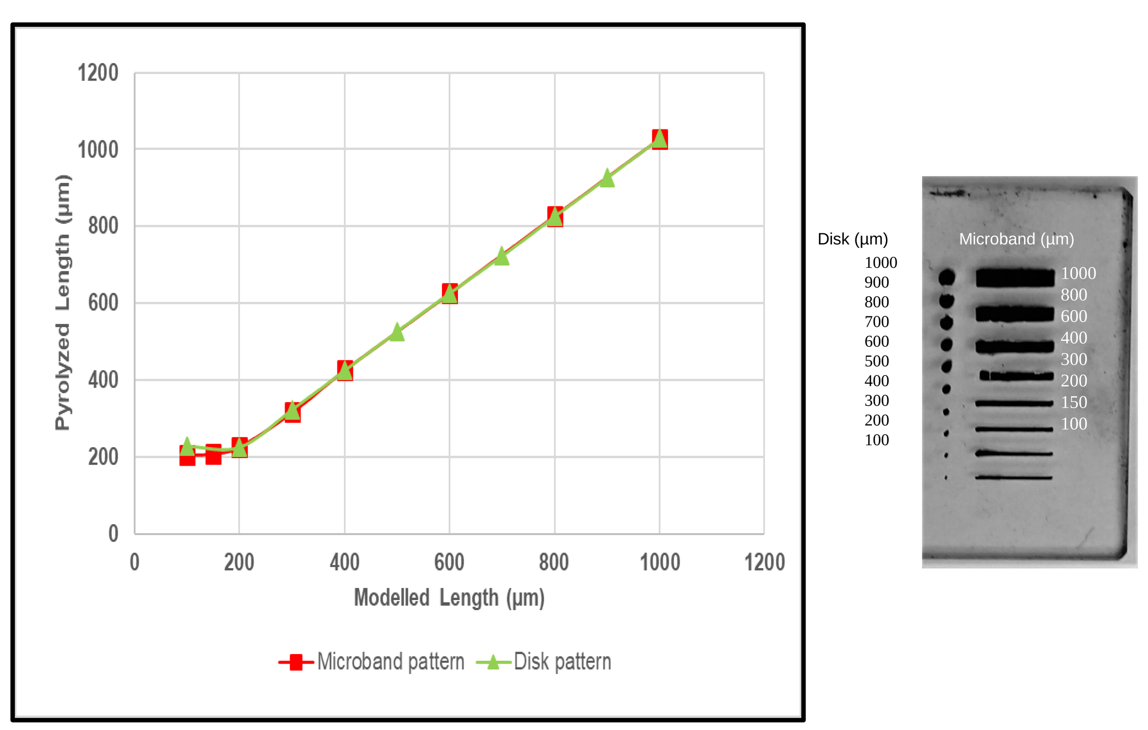


Figure 2. A research grade optical microscope was used to dimensional lengths of disk and microband electrodes pictured to the right. The points were overlaid on a graph to determine a minimum feature size that can be produced with this method. The smallest feature using this method so far is about 200 µm.

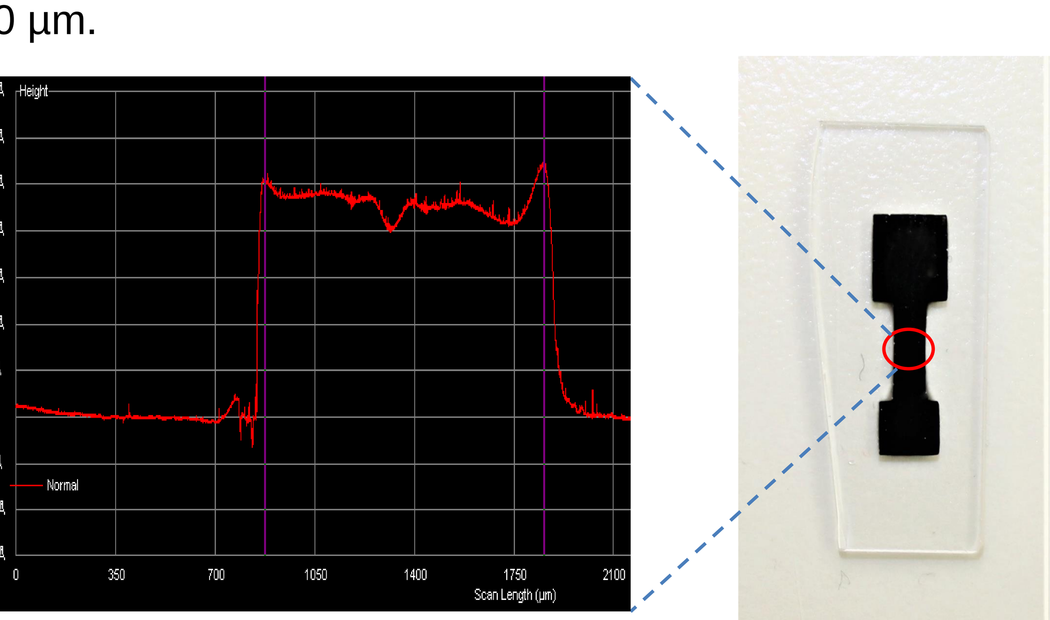
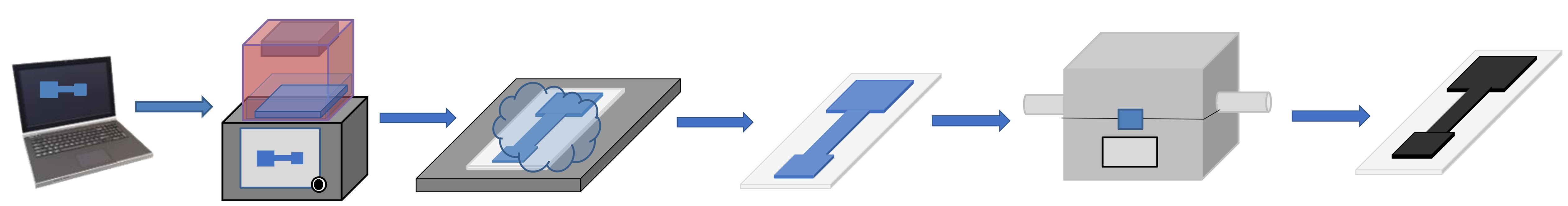


Figure 3. A step height measurement using stylus profilometry was completed on a 3D printed PPE and averaged 250 nm. A silica probe runs across the quartz and when it reaches the PPE it steps up and drags across the device until it steps done to the quartz again.

Pyrolyzed Carbon Electrode Fabrication Scheme



Briefly, computer-aided design software is used to create electrode designs, which are then 3D printed directly onto quartz slides using a photopolymerizable resin. With the 3D printer forming solid parts with an approximately 140 µm diameter laser beam, small electrode sizes are readily achieved. Next, excess resin that has not solidified is removed from the quartz slide with a 15-second isopropyl alcohol bath prior to completing the solidification process in an ultraviolet oven. The slide is then transferred to a tube furnace and pyrolyzed, which yields an electrode that behaves similar to glassy carbon.

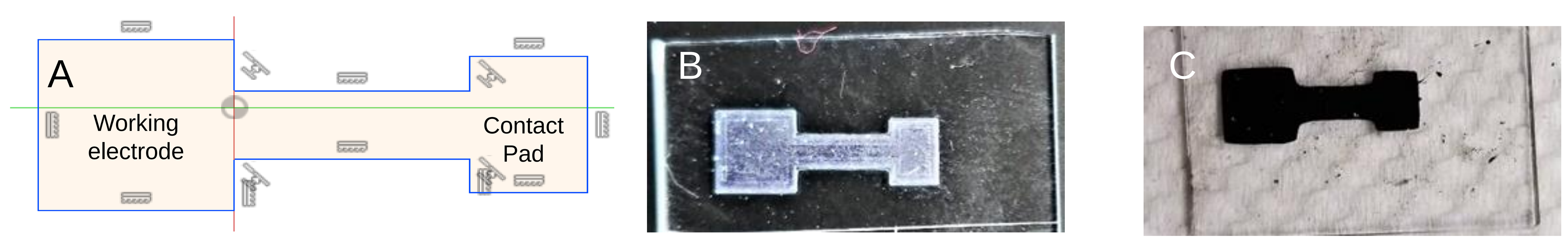


Figure 4. (A) A computer-aided design of a planar electrode for proof-of-concept studies followed by the 3D printed designs before (B) and after pyrolysis (C) supporting that 3D printed designs can be pyrolyzed using the fabrication scheme above.

Cyclic Voltammetry

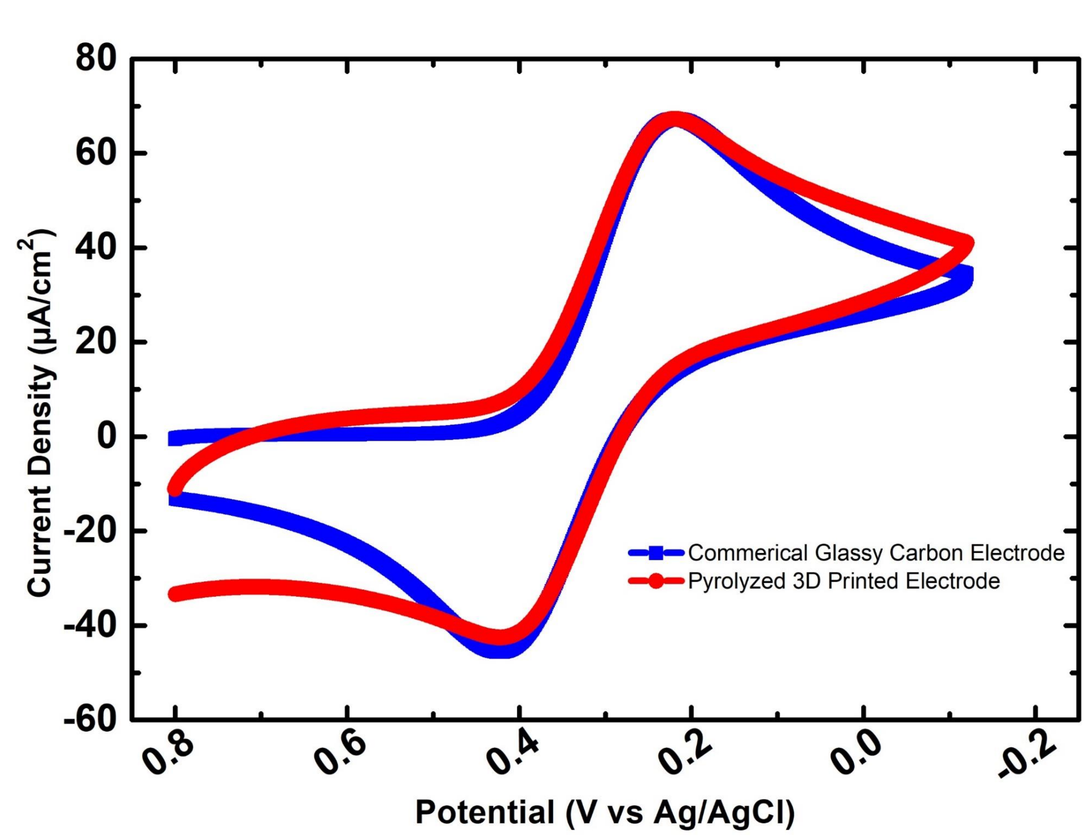


Figure 5. Cyclic voltammograms of a commercial glassy carbon electrode (blue) and a pyrolyzed 3D printed electrode (red) collected in a 4 mM potassium ferricyanide and 1.0 M potassium nitrate solution at a scan rate of 100 mV/sec with a Ag/AgCl reference electrode and Pt counter electrode.

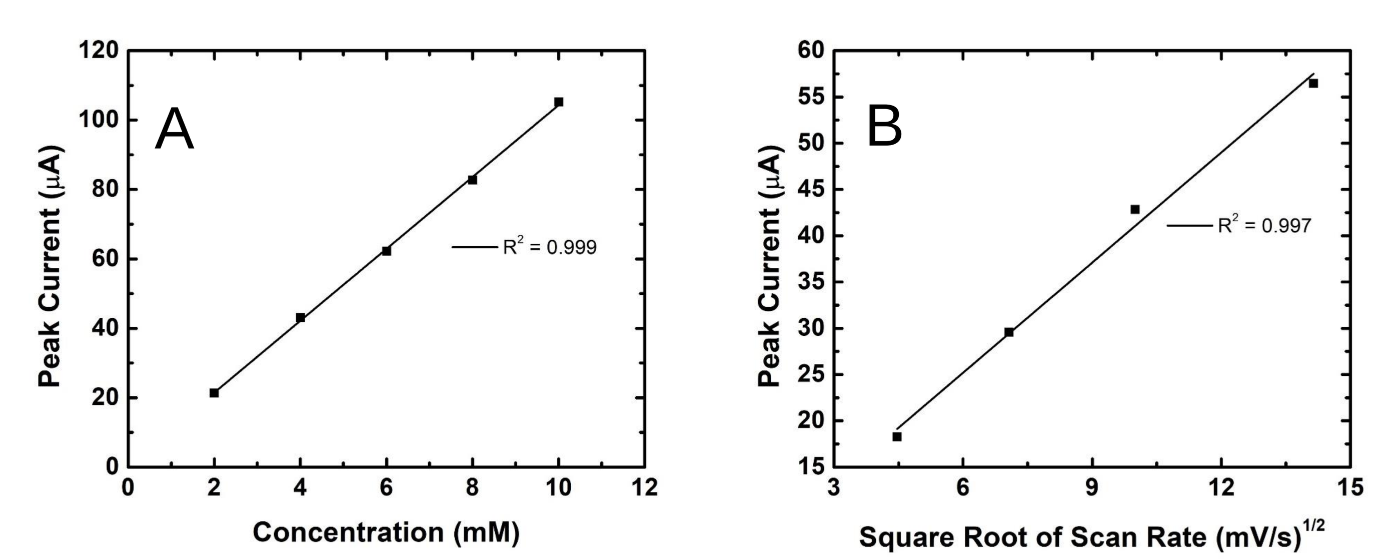


Figure 6. (A) Plot of peak current vs potassium ferricyanide concentration and (B) plot of peak current vs the square root of scan rate for cyclic voltammograms collected with a pyrolyzed 3D printed electrode, Ag/AgCl reference electrode, and Pt counter electrode. 1.0 M potassium nitrate supporting electrolyte was used for all cyclic voltammograms. Each plot demonstrates a linear relationship as predicted by the Randles-Sevcik equation.

Randles-Sevcik Equation

$$i_p=(2.687\times10^5)n^{3/2}v^{1/2}D^{1/2}AC$$

Surface Roughness

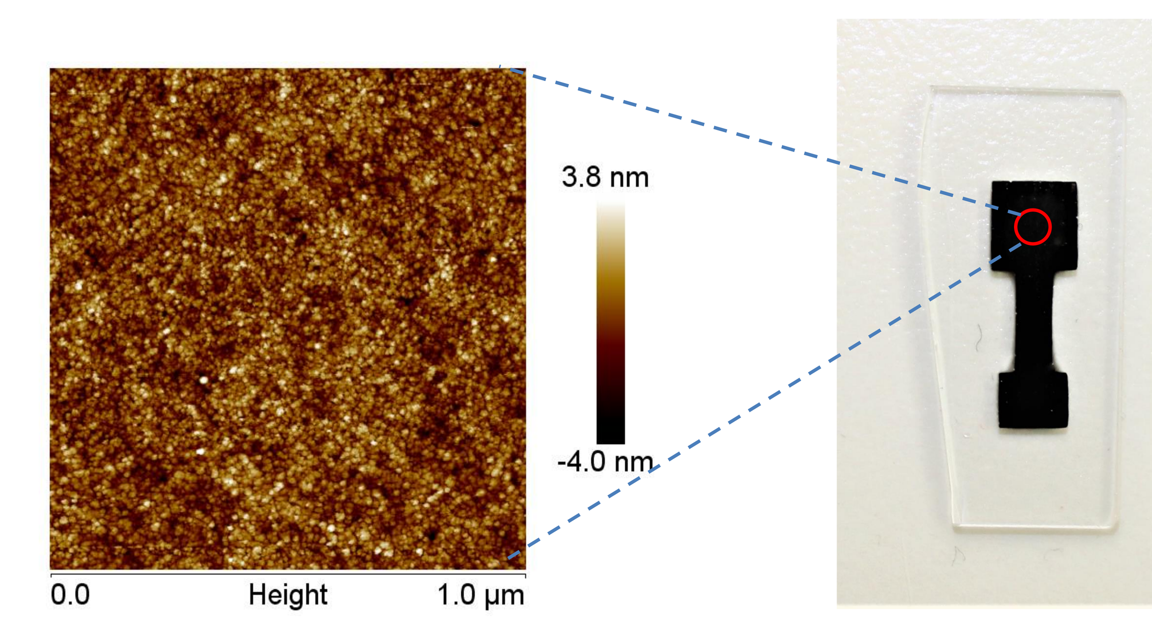


Figure 7. A surface roughness analysis was completed on a PPE device using atomic force microscopy (AFM). A silica probe was swept across a 1 micrometer X 1 micrometer area to determine a surface roughness of 1.8 nm on the device as a preliminary result. This measurement is similar to a commercial glassy carbon electrode.

Future Work

Future work including pressure driven flow electrochemistry using a 3D printed microchannel (Fig. 6), conductivity measurements with a 4-point probe, and Raman spectroscopy to determine carbon hybridization in the pyrolyzed electrode. Moreover, in addition to the planar electrodes presented here, we are working to produce electrodes having three dimensions as shown in Figure 7.

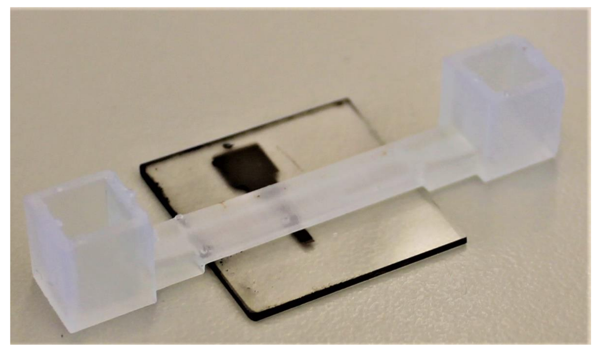


Figure 8: A 55 cm long device with a 0.3 cm x 3 cm channel and two wells. There is also a 26 mm gap in the bottom of the device where the electrode

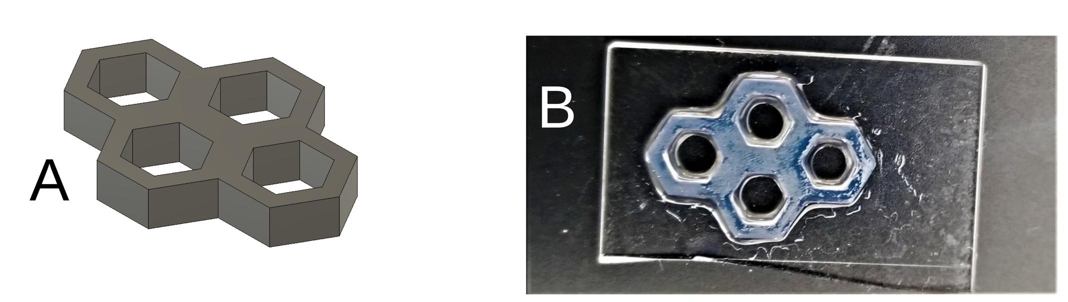


Figure 9. (A) Computer-aided design of a honeycomb electrode structure. (B) 3D printed honeycomb structure.

Acknowledgments

- Millikin University Funding
- The Beckman Institute for Advanced Science and Technology