

MATERIAL AND ELECTROCHEMICAL PROPERTIES OF PYROLYZED PARYLENE-C

Scott Miserendino[†], Stacey Boland[‡], Yu-Chong Tai[†]
[†]Caltech Micromachining Lab

[‡]Solid State Ionics and Electroceramics Research Group
 California Institute of Technology, Pasadena, CA 91125-9300, USA

Of particular interest in the microelectromechanical systems (MEMS) community is the ability to fabricate thin-film carbon microelectrodes for integration into a variety of chemical and biochemical sensors. The carbon films must be compatible with standard MEMS processing, most importantly photolithography, and still maintain all the electrochemical benefits of carbon. Pyrolyzed parylene-C not only meets these requirements but it is also conformal over high aspect ratio structures. Conformal carbon coating could be used to make high effective surface area electrodes by coating high aspect ratio structures (Fig. 1).

A free standing film of parylene-C (15.8mg) was examined by simultaneous thermal analysis, which provides thermogravimetric analysis and differential scanning calorimetry. The sample was heated to 1500°C with a heating rate of 5°C/min in flowing Ar (100mL/min). As seen in Fig. 2, the material undergoes an endothermic phase transition, presumably melting, at 296°C. An exothermic event peaks near 480°C, and is accompanied by a weight loss of 66%. Total weight loss to 1500°C is 70.1%.

MicroRaman analysis was conducted on both loose film and attached parylene samples (Fig. 3). Parylene carbonized at 900°C on Si shows broad and poorly defined G and D1 peaks, whereas carbonization at 1550°C in flowing Ar resulted in narrow and well-defined peaks, clearly indicative of glassy carbon. The band near 1580cm⁻¹ is known as the graphite band (G band) and corresponds to the in-plane vibration of C atoms in graphite structure [1, 2]. For perfect single crystal graphite, it would be the only band observed. The presence of the so-called defect band (D1) around 1350cm⁻¹ indicates that a finite particle size is associated with carbonized parylene. The D1 band is broader for poorly ordered carbons, and narrows as increased heat treatment results in increased order.

Thin-film pyrolyzed parylene-C electrodes were fabricated using room temperature polymer vapor deposition onto a Si/SiO₂ substrate. The electrodes were pyrolyzed in a nitrogen atmosphere then patterned using O₂ plasma. The 900°C electrodes were then isolated with a second parylene layer and metal contacts were deposited. Figure 4 shows cyclic voltammograms of 5 mM Fe(CN)₆^{3-/4-} in 0.1 M KCl for various processing parameters of the pyrolyzed parylene as well as a scan using a Pt electrode for comparison. Improvements in electrode kinetics, evident by a reduction in peak-to-peak separation, can be observed as carbonization temperature and film thickness are increased.

References

1. O. Beyssac, B. Goffe, et. al, "On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy," *Spectrochimica Acta Part A*, 59 2267-76 (2003).

2. F. Tuinstra and J. L. Koenig, "Raman spectrum of graphite," *J. Chem. Phys.*, 53 [3] 1126-30 (1970).

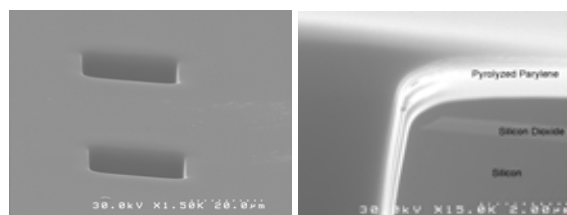


Figure 1. (left) 25 um square wells coated in pyrolyzed parylene. (right) Cross-section of the edge of a well.

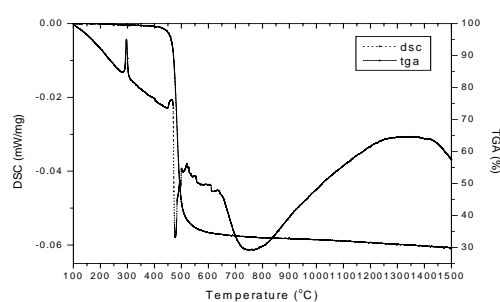


Figure 2. Simultaneous thermal analysis data for parylene C (heating rate = 5°C/min, in flowing Ar at 100mL/min)

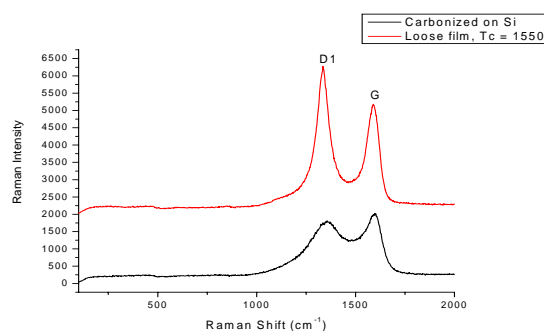


Figure 3. MicroRaman data for parylene C carbonized in furnace at 1550C (top - heating rate = 5°C/min, held at temperature for 5 minutes, flowing Ar @ 100mL/min) and parylene C carbonized on Si (heating rate = 10°C/min, held at 900°C for 1 hour, flowing N₂ at 100 mL/min) showing clear glassy carbon peaks, labeled D1 and G, according to [1, 2]

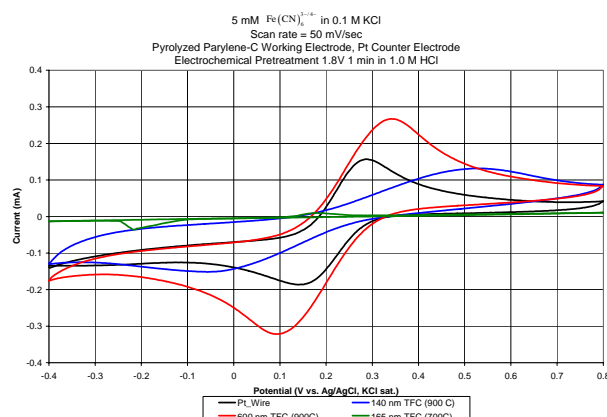


Figure 4. Cyclic voltammograms of hexacyanoferrate in potassium chloride using platinum and pyrolyzed parylene electrodes.