

Structural Influence of 3D Pyrolyzed Carbon Electrodes on Electrochemical Behavior

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One of the advantages of interferometric lithography is the ability to create 3D structures with sub-micron length scales not possible using conventional lithography. Recently, we have demonstrated that 2D and 3D submicron photoresist structures created using interferometric lithography can be converted to amorphous carbon via pyrolysis in a reducing atmosphere^{1,2}. Electrodes formed from these pyrolyzed structures show qualitatively similar electrochemical performance to standard glassy carbon electrodes, however the behavior is modified in several ways by the submicron structure.

Figure 1A shows a scanning electron micrograph (SEM) of lithographically defined 3D carbon matrix decorated with palladium nanoparticles deposited from an aqueous solution. The Pd particles are inhomogeneously distributed throughout the 3D scaffold due to the hydrophobic structured carbon. Hydrophobicity can occur either due to surface structure (e.g. silica aerogels) or surface chemistry (Teflon). These pyrolyzed electrodes possess both submicron surface roughness as well as inherent material surface hydrophobicity. Figure 1B shows an SEM image of an identical carbon scaffold decorated with Pd nanoparticles from an organic solvent solution, avoiding the hydrophobicity. While the morphology and density of the NPs are different, the NPs are distributed homogeneously through the of the matrix.

Figure 2A contains a plot of the peak anodic current versus the square root of the scan rate, while the inset plot contains two cyclic voltammograms taken at 5 and 50 mV/s (red and blue curves respectively). Over the range from 5 to 20 mV/s, the current is approximately constant, transitioning to a linear dependence on scan rate after 20mV/s. The plateau in anodic current at low scan rates is indicative of hemispherical diffusion. This is further supported by the inset voltammograms – the voltammogram at 5 mV/s is “S” shaped while the voltammogram at 50mV/s is peaked. Hemispherical diffusion, typically associated with micro electrodes, results in increased mass transport, and hence is a potential advantage, combining the increased mass transport behavior of micro electrodes with the larger surface area of an electrode $\sim 1\text{cm}^2$. This paper will present detailed fabrication and electrochemical characterization data of these materials.

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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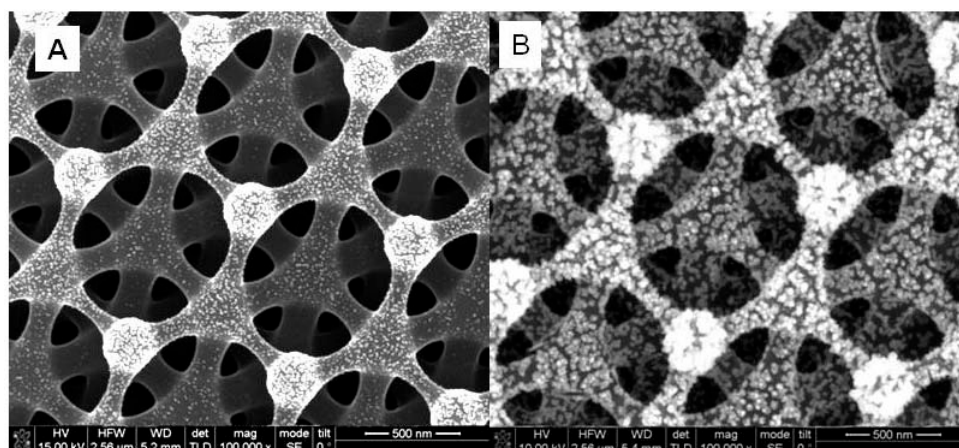


Figure 1. (A) 3D carbon scaffold decorated with Pd NPs from an aqueous solution (2mM Pd/0.5 M H₂SO₄). (B) 3D carbon scaffold decorated with Pd NPs from an organic solvent solution (2mM Pd/(MeCN + H₂O + 0.1 M HCl)).

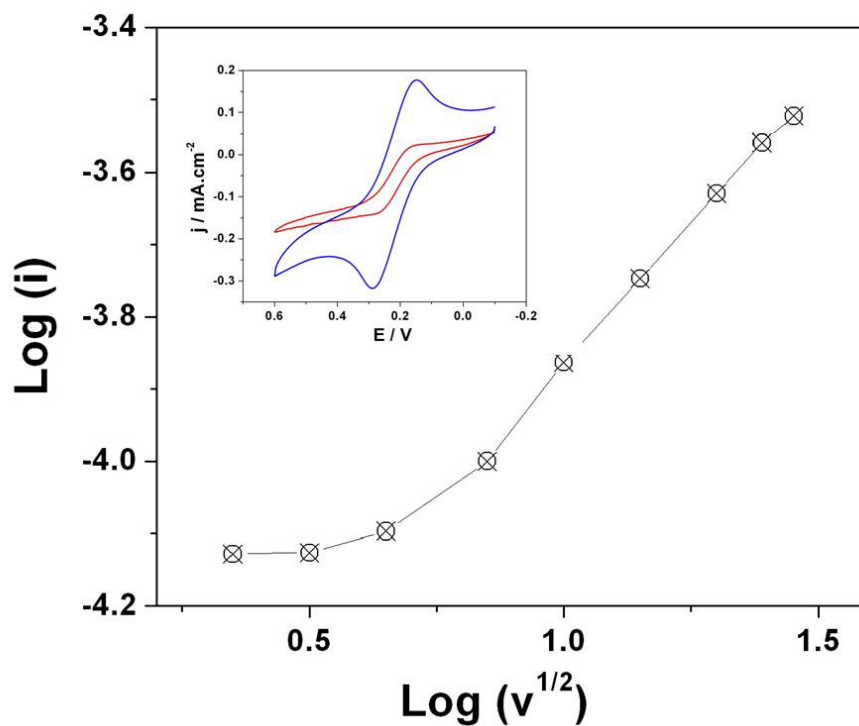


Figure 2. Plot of log current (i) versus log square root of scan rate. Inset: Cyclic voltammograms of 3D porous carbon electrodes at 5 and 50 mV/s (red and blue lines respectively). The rate independent current plateau at low scan rates and “S” shaped voltammograms are indicative of hemispherical diffusion.