Enhanced Reactivity of Nitrogen Doped Carbon Nanofibers for Dioxygen Reduction

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The synthesis of carbon nanofiber (CNF) electrodes produced by chemical vapor deposition (CVD) is demonstrated in this presentation. Stable inclusion of heteroatoms in the CNF structure is possible by this method, allowing CNF chemical reactivity to be altered and enhanced as compared to conventional non-doped CNFs. Specifically, it is shown nitrogen doped (N-doped) CNFs exhibit increased catalytic activity for the reduction of aqueous dioxygen and the decomposition of hydrogen peroxide. Prelimary data for other heteroatom doping in CNFs are also demonstrated.

Figure 1 shows a representative SEM image of "as grown" N-doped CNF electrodes where an unblemished, homogeneous film of CNFs was grown on a nickel mesh support. Electrochemical data are presented which suggest that oxygen reduction at N-doped CNF electrodes can be treated as a catalytic regenerative process where H_2O_2 is chemically decomposed to regenerate oxygen.

$$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^- \quad [1]$$

$$HO_2^- \rightleftharpoons \tfrac{1}{2}O_2 + OH^- \quad [2]$$

The proposed electrocatalysis mechanism for dioxygen reduction is supported by the observed accelerated decomposition rates of hydrogen peroxide on N-doped CNFs as compared to the activity of non-doped graphitic carbons. Rate constants for heterogeneous decomposition are reported as measured both by traditional bulk methods (1) such as rotating disk electrode voltammetry and gasometry and by a novel spectroelectrochemical approach. (2) Preliminary modeling of aqueous oxygen reduction processes with a catalytic regenerative follow-up reaction suggests that the decompostion rate constant, k_{het}, at active electrodes must be higher than that observed through bulk methods. Heterogeneous reactions are strongly dependent upon the nature of the interface and fractional coverage of reaction species, both of which may significantly vary at more extreme potentials than at open circuit. (3) Hence, the heterogeneous decompostion rate may exhibit a potential dependence near the oxygen reduction potential, i.e. the rate increases at more negative potentials.

The presented spectroelectrochemical method affords the opportunity to sensitively measure the heterogeneous chemical reaction rate while under potential control. In this approach, $Ru(bpy)_3^{2+}$ fluorescence quenching by oxygen from Reaction 2 is used to measure the consumption of hydrogen peroxide via Reaction 2. $Ru(bpy)_3^{2+}$ fluorescence is known to be an effective marker of dissolved oxygen concentration. (4) As demonstrated in Figure 2, injected hydrogen peroxide decomposes at a N-doped CNF electrode, increasingly quenching $Ru(bpy)_3^{2+}$ fluorescence as Reaction 2 proceeds over time. The observed quenching rate is seen to vary with applied potential, indicating that Reaction 2 has some potential dependence.

In addition, relevant structural features of N-doped CNFs analyzed with raman and XPS techniques are discussed and efforts to increase nitrogen doping levels are presented.

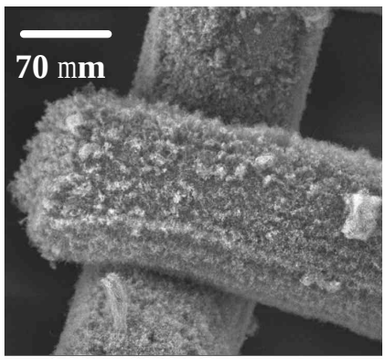

Figure 1. SEM micrograph depicting CNF film as grown on nickel mesh substrate.

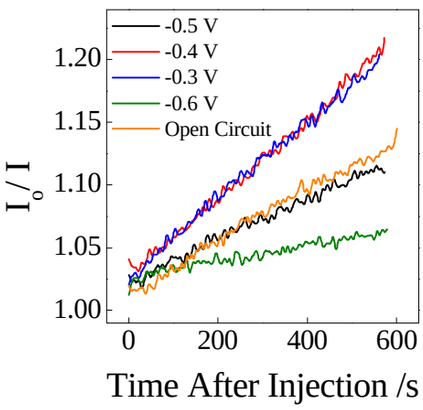

Figure 2. Spectroelectrochemical experiment for determining H_2O_2 decomposition rate constant at several different N-doped CNF electrode potentials. $Ru(bpy)_3^{2+}$ fluorescence quenching as a function of time following an injection of H_2O_2: 1 M KNO_3, 1 μm $[Ru(bpy)_3(H_2O)_6]Cl_2$, λ_{ex} = 455 nm, λ_{EM} = 600 nm, 10 mM H_2O_2, V = 3.5 mL, E vs. Hg/Hg_2SO_4,

References.

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