Method for Covalently Attaching and Site-Isolating Molecular Catalysts on Carbon Electrodes

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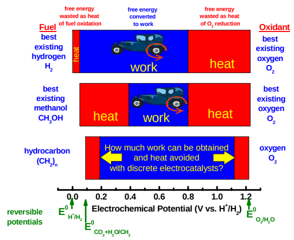
Towards More Energy Efficient Conversions

- Electrochemical oxidation of long-chain hydrocarbons $(CH_2)_n$ and reduction of oxygen using electrocatalysts at low temperatures could be the most effective way to convert fuel to mobile power
- Other electrocatalytic processes promise improved energy efficiency (oxidation of water, transformations of commodity chemicals etc.)

Electrocatalyst Efficiency



Polymer-Electrolyte-Membrane Fuel Cell

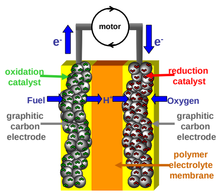


Figure 1: A schematic of Polymer-Electrolyte-Membrane (PEM) fuel cell with molecular electrocatalyst modified carbon electrodes.

Molecular Electrocatalysts on Carbon Electrodes

- Current PEM-cell electrocatalysts are noble metal nanoparticles – limited ability to tailor reactivity
- Our research aims in using coordination complexes of one or a few metal atoms covalently attached to graphitic carbon.

Modifying carbon surfaces

Important requirements:

- site-isolation of molecular catalysts on the surface
- high surface coverage
- adequate electrical coupling between the carbon surface and the molecular catalyst

Strategy for surface modification:

- aromatic nitration of graphitic carbon is identified as a method to introduce nitro groups in a site-isolated fashion.
- conversion of nitro groups to amines permits coupling to carbonyl chloride-terminated molecular catalysts through a robust amide linkage.

Useful features of nitration in surface modfication

- aromatic nitration is self-limiting due to the deactivating effect of aromatic nitro groups on subsequent nitration and leads to site-isolated introduction of nitro groups.
- nitro groups can be converted into amine groups by chemical as well as electrochemical methods.
- presence of nitro and amine groups can be detected by X-ray photoelectron spectroscopy (XPS).
- amine-modified carbon surfaces can be used to couple carbonyl chloride terminated molecular catalysts as shown in Figure 2.

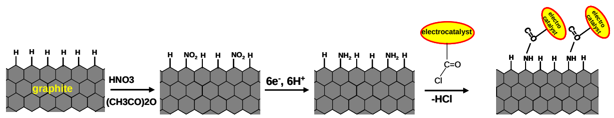


Figure 2: Schematic diagram of nitration and subsequent modification of graphitic edges with electrocatalysts.

Nitration of carbon surfaces with nitric acid and acetic anhydride* mixtures - XPS studies

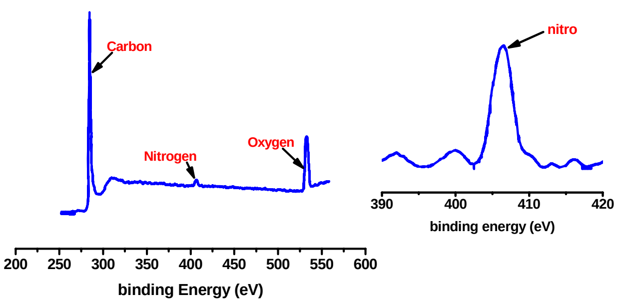


Figure 3: XPS data of a carbon surface nitrated using 63:37 mixture of nitric acid:acetic anhydride. (inset shows the zoomed nitrogen region)
* acetic anhydride is used as a dehydrating agent

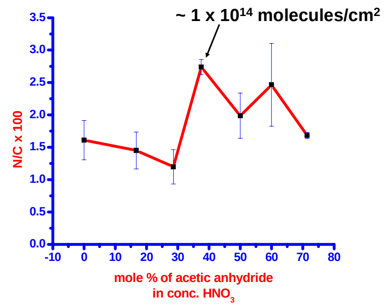


Figure 4: Plot of variation of nitrogen to carbon ratio obtained from XPS as a function of mole percentage of acetic anhydride in conc. nitric acid.

Conversion of nitro to amine:

- sodium dithionite ($Na_2S_2O_4$) is used to reduce nitro groups into amine groups.
- conversion of nitro groups to amine groups can be followed by the absence of peak at 406 eV (nitro) and appearance of peak at 400 eV (amine) by XPS.

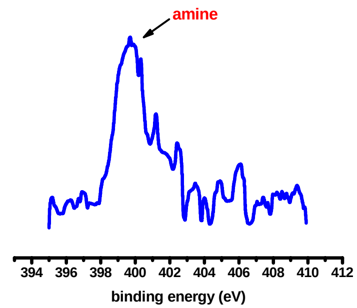


Figure 5: XPS data showing the presence of amine groups on the nitrated carbon surfaces treated with sodium dithionite.

Conclusion: A method to introduce site-isolated reaction centers on carbon surfaces to which molecular catalysts can be covalently coupled is developed by aromatic nitration. The presence of nitro groups and amino groups is confirmed by XPS technique. Further work on coupling carbonyl chloride containing electrocatalyst to the amine terminated carbon surfaces are underway.

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