Advanced Carbon Material for Energy and Electroanalytical Application

Doo Young Kim, Ph.D.
Department of Chemistry
University of Kentucky

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My Research

PEM Fuel Cells

Supercapacitor with Fast Ion Access!!

Electroanalysis

Fluorescent Organic Nanoparticle

Electroanalysis

Supercapacitor with Fast Ion Access!!

Fluorescent Organic Nanoparticle

Supercapacitor with Fast Ion Access!!

Fluorescent Organic Nanoparticle
1. Advanced Carbon-Support Material in Proton Exchange Membrane (PEM) Fuel Cells
   - Current challenge and development of advanced carbon support

2. Electrochemical Modification of Graphene Material
   Tailoring the electrochemical property of graphene
Advanced Electrodes for Fuel Cells

Polymer Electrolyte Membrane Fuel Cell

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
<th>Overall</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- )</td>
<td>( \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>( \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
</tr>
<tr>
<td></td>
<td>( E^\circ = 0.000 \text{ V} )</td>
<td>( E^\circ = 1.229 \text{ V} )</td>
<td>( E^\circ = 1.229 \text{ V} )</td>
</tr>
</tbody>
</table>

For a fuel cell operating at thermodynamic equilibrium:

\[ \Delta G = -nF\Delta E^\circ \]

Efficiency limitations:
- Resistance
- Loss of electrocatalyst
- Overpotential

Use of stable electrodes and interfaces is key!

Membrane-Electrode Assembly (MEA)

PEM-FC

Membrane-Electrode Assembly (MEA)

Pt Catalyst / Carbon Support

Carbon
Black

Pt
Durability Problem: Carbon Support Corrosion

\[ \text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad E = 0.207 \text{ V vs. RHE} \]

- During start-up/shut-down, high potential \((E \sim 1.4 \text{ V})\) is experienced at cathode, causing carbon corrosion.
- **Alternative electro-catalyst supports are needed with improved microstructural stability and corrosion resistance.**

Durability Problem: Carbon Support Corrosion

**Microstructural Changes**

- Loss of Carbon
- Loss of Electrocatalyst
- Increased Ohmic Resistance

**Surface Oxidation**

Corrosion ($\text{CO}_2$)

Decrease Fuel Cell Efficiency
Our Approach: \(\text{sp}^2/\text{sp}^3\) Carbon Composite

Conducting Diamond - Coated \(\text{sp}^2\) Carbon Powders

\[\text{CH}_4/\text{H}_2/\text{Ar}/\text{B}_2\text{H}_6\]

Chemical Vapor Deposition

- GC = Glassy Carbon
- B-UNCD = Boron-doped Ultra-nanocrystalline Diamond
Why is Diamond for Advanced Electrocatalyst Support?

- Wide electrochemical window
- Very low background intensity
- Chemically inert surface
- Microstructurally stable for electrochemical oxidation
- Requirement
  - High conductivity ( > 1 S/cm)
  - High surface Area ( > 100 m²/g )

Ar-rich plasma, microwave-assisted CVD for UNCD growth
UNCD= ultra-nanocrystalline diamond
10 ppm of $\text{B}_2\text{H}_6$, $\text{Ar} : \text{CH}_4 : \text{H}_2 = 94 : 1 : 5 \text{ sccm}$
Power = 800 W, pressure = 140 Torr
1. Diamond-coated GC (B-UNCD-GC)

- Uniform growth of Diamond Overlayer on glassy carbon powders!!
- B- UNCD has a nodular structure

Characterization of GC and B-UNCD-GC

Raman Spectra

Intensity (arbi. units)

Raman Shift (cm$^{-1}$)

800 1000 1200 1400 1600 1800
1333 cm$^{-1}$ 1550 cm$^{-1}$
1350 cm$^{-1}$ 1580 cm$^{-1}$
1150 cm$^{-1}$

X-ray Diffraction

Intensity (arbi. units)

2-Theta (degrees)

20 30 40 50 60 70 80 90 100
G (002) G (100) G (004) G (110)
G (002) G (004) G (110)
Hydrogenated GC: Stage of Diamond Nucleation

- First, hydrogenation occurs on GC surface, and make hydrogenated GC (HGC), which is shown as ridges in the figure above.
- Second, diamond nucleates on the HGC surfaces
2. Microstructure of Ketjen Black (KB)

- Specific BET surface area of ~ 800 m²/g
- Shell is ordered (graphitic) and core is more disordered and amorphous.
- Small graphitic crystallites ($L_a = 3$ nm, $L_c = 1$ nm)
After B-UNCD coating, the powder showed typical Raman spectra of ultra-nanocrystalline diamond (UNCD).
• Interface between Ketjen Black and diamond is observed
• Diamond nucleates at exposed edge plane of Ketjen Black and continues to grow
• Graphene layer is opened-up to allow for the diamond growth (hydrogenation)
• 3 graphene layers ((002) plane) are matched with 4 diamond layers ((111) plane)
TEM images showed well dispersed Pt on KB and B-UNCD-KB.

XRD showed mixed phases of diamond and Pt.

At Pt loading of 15 wt %, Pt size was ~ 3 nm.
20 wt % Pt impregnated on KB and B-UNCD-KB
ADT : 1.4 V vs. RHE in 0.5 M H$_2$SO$_4$ (5 h, 80 °C)
Pt-KB : 67 % loss in activity (76 to 25 m$^2$/1g$_{Pt}$)
Pt-UNCD-KB : 14 % loss in activity (73 to 63 m$^2$/1g$_{Pt}$)
Charge : Pt-KB (4.9 C/mg$_C$), Pt-UNCD-KB (0.97 C/mg$_C$)
Corrosion rate : Pt-KB (31 µg/mg·h), Pt–UNCD-KB (6.1 µg/mg·h)
**XRD Study of Pt Particle Size Change after ADT**

<table>
<thead>
<tr>
<th>Pt loading (wt %)</th>
<th>Pt size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>10</td>
<td>4.2</td>
</tr>
<tr>
<td>15</td>
<td>4.7</td>
</tr>
<tr>
<td>20</td>
<td>7.4</td>
</tr>
<tr>
<td>15*</td>
<td>4.0*</td>
</tr>
</tbody>
</table>

- ADT : 1.4 V vs. RHE in 0.5 M H₂SO₄ (80 °C, 5 h)
- Pt size was calculated from Pt (220) peak using Scherrer equation.
- Pt-UNCD-KB showed negligible Pt size change (<1 nm), whereas Pt-KB showed significant increase (~2x).
Summary I

- Glassy carbon (GC) and Ketjen Black (KB) powders were coated with boron-doped ultra-nanocrystalline diamond (B-UNCD) overlayer by microwave-assisted chemical vapor deposition (MA-CVD).

- Diamond initially nucleates at exposed graphitic edge plane sites.

- UNCD overlayer imparts a high level of corrosion protection and microstructural stability to KB.

- Anodic charge passed during the accelerated degradation test for B-UNCD-KB is 6x less than for KB (4.9 vs. 0.97 mC/mg$_C$).

- Negligible change in Pt particle size or Pt activity on B-UNCD-KB after ADT.
Probing the Electrochemical Properties of Graphene
What is Graphene?

- Single atom-thick, sp²-carbon.
- Semi-metal or zero-band gap semiconductor
- Excellent electrical conductivity: electron mobility of 20,000 cm²/(Vs) at RT
- High BET surface area: single graphene has ~ 2600 m²/g
- Electrochemical stability and activity: catalyst support, electrochemical sensor
Graphene-based Devices

Graphene FET Device


Graphene supercapacitor

BET surface area ~ 700 m²/g
Capacitance ~ 100 F/g, Fast charging

Optically Transparent Electrode (OTE)


Metal-decorated GNP

ACS Nano (2009)
Multilayer Graphene Nanoflakes Grown by CVD


Figure 1. SEM images of MGNFs deposited for 40 s (a) and 30 min (b); (c) is an enlarged image of (a); (d) is a cross sectional SEM image of MGNFs deposited for 30 min; (e) is an enlarged image of (d), showing the nanoflake preferentially vertical to the Si substrate.

Carbon nanowall

GNP-coated GC

GNP-grown on KB
Study Objectives

1. Understand Electronic Properties and Related Electric Double Layer Structure of Graphene

2. Inhomogeneity of Electrochemical Activity (Role of Basal Plane & Edge Plane) - Spatially Resolved Electrochemical Study

3. Modified Graphene to maximize its usage for Electro-analytical Application
Optically Transparent Graphene Electrode

- Graphene placed on transparent substrate
- Multi-layered graphene segments
- Distribution of graphene microstructure, size.

Height

Deflection

glass

graphene sheet
Transmittance is an accurate tool to measure the number of graphene layers. For each single layer, transmittance dropped simply by 2.3%.
• The peak shape of 2D band is similar to the Raman peak of 10 layers in reference.
Spatially Resolved Electrochemical Activity of Graphene: Electrochemical Microscopy (SECM)

1mM Mediators
Ru(NH₃)₆²⁺/³⁺
Fe(CN)₆⁴⁻/³⁻

Tip radius c.a. 5 µm

substrate

(A) diffusion-limited current in bulk solution

O

O

O

O

R

O

O

(B) negative feedback

insulating substrate

O

O

R

O

(C) positive feedback

conductive substrate
Electron transfer kinetics with Ru(NH$_3$)$_6$ redox couple is determined by the electrode conductivity and density of states (DOS).

Ferro-cyanide showed a long-range heterogeneity in electrochemical activity, indicating the effect of edge-plane density.

\[ i_\infty = 1.9 \text{ nA} \]
Most region is shown as P.F.

\[ i_\infty = 1.2 \text{ nA} \]
Most region is shown as N.F.
Surface Modification of Graphene

- Change in electronic structure
- Hydrophilicity, hydrophobicity
- Surface interaction with analyte
- Electrochemical property
- Sensor property: sensitivity & selectivity
Electrochemical Modification of Graphene

\[
\text{R-C}_6\text{H}_4-\text{N}_2^+ + \text{e}^- \rightarrow \text{N}_2 + \text{R-C}_6\text{H}_4^\cdot \quad (\sim 0.4 \text{ V vs. Ag/AgCl})
\]

Graphene + R-C\text{C}_6\text{H}_4^\cdot \rightarrow \text{Graphene-C}_6\text{H}_4-\text{R}

R = \text{NO}_2

Edge plane vs. Basal plane
• Derivatization process by reverse sweep of CV, scan rate = 5 mV/s
• 5 mM 4-nitrobenzene diazonium tetrafluoroborate in 0.1 M acetonitrile + tetrabutylammonium tetrafluoroborate
• Background CV after derivatization, 100 mV/s showed reversible redox reaction of nitro group
• Reduced capacitive current
• Suppressed electron transfer kinetics for both Fe(CN)$_6$ and Ru(NH$_3$)$_6$
Further Change from -NO₂ to –NH₂

CV in 0.1M KCl in EtOH / H₂O (1/9) at 50mV/s

Chemical equations:

\[
\text{NO}_2^- + 6\text{e}^- + 6\text{H}^+ \rightarrow \text{NH}_2 + 2\text{H}_2\text{O}
\]
- Positive charge on the electrode at low pH (1 M H₂SO₄)
- Kinetics becomes faster for Ferro, and is suppressed for Ruhex because of electrostatic interaction between redox analyte and electrode surface
- Selectivity in electron transfer kinetics
• Basic Characterization (optical, Raman, AFM, SEM)

• SECM showed spatial inhomogeneity for both Fe(CN)$_6$$^{4/-3}$ and Ru(NH$_3$)$_6$$^{2+/3}$

• Graphene electrode was modified with aryl group by electrochemical method, and nitro-group- modified electrode showed the blocking effect and amine-modified electrode showed the selective change of electron transfer kinetics according to the charge.
Planned Studies

- Utilizing sp$^2$/sp$^3$ Composite catalyst support and metal-oxide-diamond catalyst support for PEM Fuel Cell
- High Energy density, Power density Energy Storage Device
- Modified Graphene Electrode to optimize the sensitivity and selectivity
- Basic electrochemical characterization of carbon powders