High Energy Density Ultracapacitors Based on GUITAR-Nanospring Composites

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GUITAR

• Graphene from the University of Idaho Thermolyzed Asphalt Reaction

• Excellent Electrochemical Characteristics
  – $10^1$ to $10^8$ faster than graphene for heterogeneous electron transfer
  – Wide aqueous potential window, 2 - 3 volts vs. 1 volt for Activated Carbon
  – High capacitance, 1000 vs. 10 μF/cm² for Activated Carbon
GUITAR is not Graphite or Graphene

- **GUITAR Electrodes**
  1. Fast Heterogeneous Electron Transfer.
  2. High Corrosion Stability
  3. High Hydrogen Overpotential
  4. Resistant to $O_2$ oxidation
  5. High Capacitance, up to 1000 $\mu$F/cm$^2$

- **Graphite and Graphene**
  1. Slower Heterogeneous Electron Transfer, up to $10^{-10}$
  2. Corrosion, 0.5 volts lower
  3. $H_2$ over potential 0.5 lower
  4. Much more susceptible
  5. Capacitance 10 $\mu$F/cm$^2$
GUITAR Morphology and Characterization

• Metallic Appearance
  – Optical Microscopy, SEM, AFM and TEM
    – Indicate Flat and Layered - resembles an ordered graphitic system

• Raman Spectroscopy
  – Indicates Nano-crystalline grains of 5 nm
  – Disordered System

• IR Spectroscopy
  – 861 and 1576 cm\(^{-1}\) peaks intralayer graphene stretches
  – No other surface functionalities

• \(sp^2\) hybridized carbon
  – X-ray Photoelectron Spectroscopy
Figure. GUITAR graphene, A – a photograph of a flake approximately 25 mm in diameter. B – an optical micrograph (400x) in water. C – graphene layers (400x). D – 9.45K x SEM of microtomed layers on Si. E – 23.08K x SEM showing layered characteristics. F – A TEM showing layered characteristics on the nanometer scale.
Synthesis of GUITAR

• **Controlled combustion at 900 °C**
  – Organics MP - BP between 100 to 250 °C
  – Elemental or Organic Sulfur

• **Successful Reagents (contains S)**
  – Shale Oil
  – Crude Oil
  – Roofing Tar (Ace Hardware)
  – Taco Chips
  – Some Candy Bars

• **Failed (S free)**
  – Motor Oil, 5W-20
  – Paraffin
  – Pyrene
Mechanism of Formation

• Hunch - Sulfur is Involved

cyclohexanol and Sulfur
cyclohexanol only
Hypothesized TAR Mechanism


- Based on Cyclohexanol + Sulfur
What is GUITAR?

• Not Graphene or Highly Oriented Pyrolytic Graphite (HOPG)
  – GUITAR is too disordered

• Not “Graphene Paper”
  – GP has Wavy and Mottled Surface
  – GUITAR appears flat (SEM)

• Is GUITAR just graphite?
  – Electrochemical Characteristics indicate GUITAR is not just graphite
Electrochemical Investigations

• Graphene and HOPG are not good electrodes
  – Both have a barrier to electron transfer
  – Subject to effects of air oxidation
  – Costs

• GUITAR is an excellent electrode
  – Fast heterogeneous electron transfer rates
  – Wide electrochemical aqueous window 2 - 3 volts
  – Inexpensive
GUITAR electrode fabrication

- Vapor deposit GUITAR onto silicon wafer @ 900 °C
- Transfer the GUITAR flakes onto mica by vacuum grease or 3M double sided conductive tape

Basal Plane (BP) GUITAR

Edge plane of GUITAR sealed with paraffin wax

As-grown GUITAR revealing ‘basal’ and ‘edge’ planes
Cyclic Voltammetry Indicates that GUITAR has excellent e-transfer rates with dissolved redox couples.

$\Delta E_p = 73 \pm 5 \text{ mV}$

$n = 3$

$\Delta E_p = 69 \pm 1 \text{ mV}$

$n = 3$

1 cm$^2$, 0.1 M KCl(aq) at 50 mV/s.

$\text{Fe}^{\text{II}}(\text{CN})_6^{4-} \rightleftharpoons \text{Fe}^{\text{III}}(\text{CN})_6^{3-} + \text{e}^-$

$\text{Fe}^{\text{III}}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Fe}^{\text{II}}(\text{CN})_6^{4-}$

$\text{Ru}^{\text{II}}(\text{NH}_3)_6^{2+} \rightleftharpoons \text{Ru}^{\text{III}}(\text{NH}_3)_6^{3+} + \text{e}^-$

$\text{Ru}^{\text{III}}(\text{NH}_3)_6^{3+} + \text{e}^- \rightarrow \text{Ru}^{\text{II}}(\text{NH}_3)_6^{2+}$
Graphene and HOPG are poor electrodes

- Calculated Standard Rate Constant ($k^0$) for GUITAR Ox + ne- $\rightleftharpoons$ Red $k^0$ (cm/s)

<table>
<thead>
<tr>
<th></th>
<th>Fe(CN)$_6^{3-/4-}$</th>
<th>Ru(NH$_3$)$_6^{3+/2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUITAR</td>
<td>$1.2 \times 10^{-2}$</td>
<td>$1.7 \times 10^{-2}$</td>
</tr>
<tr>
<td>HOPG</td>
<td>$10^{-9}$ to $10^{-6}$</td>
<td>$10^{-5}$ to $10^{-3}$</td>
</tr>
<tr>
<td>Graphene</td>
<td>$10^{-10}$ to $10^{-9}$</td>
<td>$2.5 \times 10^{-3}$ to $5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Why is GUITAR a superior electrode?

• Density of Electronic States (DOS)

• Low DOS near Fermi Level for crystalline graphites
  – HOPG
  – Graphene

• Next Slide

From McCreery Table 5

<table>
<thead>
<tr>
<th></th>
<th>Free e- density (cm$^{-3}$)</th>
<th>DOS at Fermi Level states/atom/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$6 \times 10^{22}$</td>
<td>0.28</td>
</tr>
<tr>
<td>HOPG</td>
<td>$5 \times 10^{18}$</td>
<td>$2.2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
GUITAR Electrodes

• Higher DOS along Structural Defects?
• Structural Defects
  – Sites for fast e- transfer?
  – Nano-crystals 5 nm
Aqueous Potential Window

• Positive (anodic) Limit
  – Corrosion, for carbon electrodes:
    \[ C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E^0 = 0.207 \text{ V} \]
  – Water: \[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23 \text{ volts} \]

• Negative (cathodic) Limit:
  – Water: \[ 4H^+ + 4e^- \rightarrow 2H_2 \quad E^0 = 0.00 \text{ volts} \]
Aqueous Potential Window - Voltammetric Characteristics

- Important for
  - Electrochemical Detectors
  - Water Purifiers
  - Batteries
  - Fuel Cells
  - Ultracapacitors

Diagram:
- Hydrogen overpotential: $4H^+ + 4e^- \rightarrow 2H_2$
- Oxygen overpotential: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- Current
- E, potential (Volts)
- 1.23 V
Potential Windows in 1 M H$_2$SO$_4$
<table>
<thead>
<tr>
<th>Material</th>
<th>Cathodic limits (V)</th>
<th>Anodic limits (V)</th>
<th>Total Windows (V)</th>
<th>Current Limits (µA/cm²)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GUITAR</strong></td>
<td>-0.9</td>
<td>2.1</td>
<td>3.0</td>
<td>200</td>
<td>This work</td>
</tr>
<tr>
<td>Graphites†</td>
<td>-0.4 – -0.5</td>
<td>1.4 – 1.9</td>
<td>1.9 – 2.3</td>
<td>200</td>
<td>This work &amp; Literature</td>
</tr>
<tr>
<td>Synthetic Diamonds‡</td>
<td>-0.4 – -1.25</td>
<td>1.7 – 2.4</td>
<td>2.3 – 3.5</td>
<td>200 – 300</td>
<td>Literature</td>
</tr>
</tbody>
</table>

† Graphite includes; HOPG, pyrolytic graphite, glassy carbon and exfoliated graphite

‡ Synthetic Diamonds include; boron doped diamond, low and high sp² diamond and diamond-like-carbon
GUITAR Aqueous Potential Window

• 3 V in other Electrolytes, e.g. $\text{H}_3\text{PO}_4$, $\text{KNO}_3$, $\text{HClO}_4$, $\text{Na}_2\text{SO}_4$

• 3 V is Competitive with Synthetic Diamond Electrodes

• Surpasses the 2 V Windows of other Graphitic Materials
  – Glassy Carbon
  – Graphite
  – HOPG
  – Graphene
Why Does GUITAR Have a Large Potential Window?

- Cathodic Limits - Hypotheses are being developed

- Anodic Limits - GUITAR Does Not Have the Electrolyte Intercalation characteristics of other graphites.

Blister formation on graphitic anodes

- **Forward voltammetric scan**
  - 2 gas evolution reactions:
    - $2\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$
    - $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$
  - Electrolyte intercalation:
    - $[\text{C}_x] + [\text{HSO}_4^-] + y\text{H}_2\text{O} = [\text{C}_x^+ \text{HSO}_4^-]y(\text{H}_2\text{O}) + y\text{e}^-$

- **Reverse scan**
  - Electrolyte de-intercalation
    - $[\text{C}_x^+ \text{HSO}_4^-]y(\text{H}_2\text{O}) + y\text{e}^- = [\text{C}_x] + [\text{HSO}_4^-] + y\text{H}_2\text{O}$


Jan. 13, 2014
GUITAR Lacks Voltammetric Evidence for Electrolyte Intercalation

GUITAR Electrode

Pyrolytic Graphite Electrode

Potential vs. Ag/AgCl

Zero De-intercalation current

De-intercalation current

1 M H$_2$SO$_4$

20mA/cm$^2$
Cyclic voltammograms of a 1 cm² GUITAR electrode in various electrolytes at 50 mV/s. All the solutions were purged with Ar.

400 μA/cm²

GUITAR anodes do not exhibit electrolytic intercalation

Other electrolytic systems

Cyclic voltammograms of a 1 cm² GUITAR electrode in various electrolytes at 50 mV/s. All the solutions were purged with Ar.
Current Model

- HOPG anodic limit 1.7 V
- GUITAR anodic limit 2.1 V

Electrolytic penetration

Micron size grains
- Pin-Holes
- Fewer DOS

Nano-size Grains w/Structural Defects
- Pin-Hole Free?
- Higher DOS
Ultracapacitors & Energy Storage

- $E = \frac{1}{2} CV^2$
- **Energy Storage**
  - Increased Capacitance
  - Increase Cell Voltage, $V$
    - Potential window
  - Aqueous Systems Preferred
    - $\text{H}_2\text{SO}_4(\text{aq})$
- **Requires Zero Faradaic Current**
  - Charging or Capacitive only
Capacitance Studies

- GUITAR has much higher capacitance than other materials - DOS?

- Capacitors Applications Require Zero Faradaic current
  - Narrower potential window than 200 $\mu$A/cm$^2$ limits

- Cyclic voltammetric measurements
  \[ C = \frac{i}{dV/dt} \]
GUITAR proposed capacitive window -0.8V – +1.2V, 640µF/cm², @0.1V

Glassy carbon, -0.6V – +0.7V, 50µF/cm²

Pyrolytic Graphite, -0.1V – +0.65V, 7µF/cm²
<table>
<thead>
<tr>
<th>Material</th>
<th>Cathodic Limit (Volts)</th>
<th>Anodic Limit (Volts)</th>
<th>Capacitive Window (Volts)</th>
<th>Capacitance ($\mu$F/cm$^2$) @ 0.1 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>GUITAR</td>
<td>-0.8</td>
<td>1.2</td>
<td>2</td>
<td>640</td>
</tr>
<tr>
<td>Glassy Carbon (Bioanalytical Systems)</td>
<td>-0.6</td>
<td>0.7</td>
<td>1.3</td>
<td>50</td>
</tr>
<tr>
<td>Pyrolytic Graphite</td>
<td>-0.1</td>
<td>0.65</td>
<td>0.75</td>
<td>7</td>
</tr>
<tr>
<td>Activated Carbon (literature)</td>
<td></td>
<td></td>
<td>0.8 V</td>
<td>10</td>
</tr>
</tbody>
</table>

- GUITAR has more capacitance per unit than other carbon electrodes.
- GUITAR has a wider capacitive window than other carbon electrodes.
GUITAR vs. Activated Carbon (AC)

- AC — the predominate material in UC’s. Low Cost & High Surface Area

- Potential Window, & Capacitance,
  - \( C = 10 \, \mu\text{F/cm}^2 \)
  - \( V = 0.8 \, \text{V} \)

- Expected Performance:
  
  - **AC)** \( \text{Energy} = \frac{1}{2} CV^2 = 3 \, \mu\text{J/cm}^2 \)
  
  - **GUITAR)** \( \text{Energy} = 1300 \, \mu\text{J/cm}^2 \)
GUITAR vs. Activated Carbon (AC)

• AC surface area $\approx 1000 \text{ m}^2/\text{g}$
  – Specific Energy = 30 J/g

• GUITAR - produces conformal coatings
  – On McIlroy Nanosprings, surface area = 200 m$^2$/g
    – Specific Energy = 2600 J/g
    – Excluding nanospring mass
A – Bare silica McIlroy nanosprings. B – D Silica nanosprings coated with G-UI-TAR.
Proposed Applications for High Surface Area GUITAR Electrodes

- **Ultra-capacitors**
  - Aqueous Ucaps limited to 1.5 volts
  - GUITAR Ucaps > 2.0 V
  - Higher capacitance based on DOS?

- **Water Purification**
  - Wide potential and excellent electrode
  - Hydrophobic surface adsorption

- **V Redox Flow Batteries**
  - Requires high H₂ overpotential and, e- transfer kinetics

- **Enhancing Lead-Acid Battery**
  - Requires corrosion resistance, high O₂ and H₂ overpotential, conformal coatings on microporous materials, and electrochemical conductivity.

- **CNT Replacement in Fuel Cells**
  - GUITAR on nanosprings
END OF PRESENTATION
SCRATCH SLIDES
As-grown GUITAR revealing 'basal' and 'edge' planes

Scheme A

Basal Plane (BP) GUITAR

Edge plane of GUITAR sealed with paraffin wax

Scheme B

Basal plane of GUITAR sealed with paraffin wax

As-grown GUITAR revealing 'basal' and 'edge' planes

Edge Plane (EP) GUITAR

Cu clip for electrical contact

Glass substrate

GUITAR flake

Paraffin wax insulator
As-grown GUITAR revealing ‘basal’ and ‘edge’ planes

Basal Plane (BP) GUITAR

Edge plane of GUITAR sealed with paraffin wax

University of Idaho
Hydrogen overpotential

\[ 4H^+ + 4e^- \rightarrow 2H_2 \]

Oxygen overpotential

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]

No reaction

\[ E, \ \text{potential (Volts)} \]

0 V

1.23 V