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 $\mu F/cm^2$ for Activated Carbon

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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 μF/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 μF/cm^2

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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

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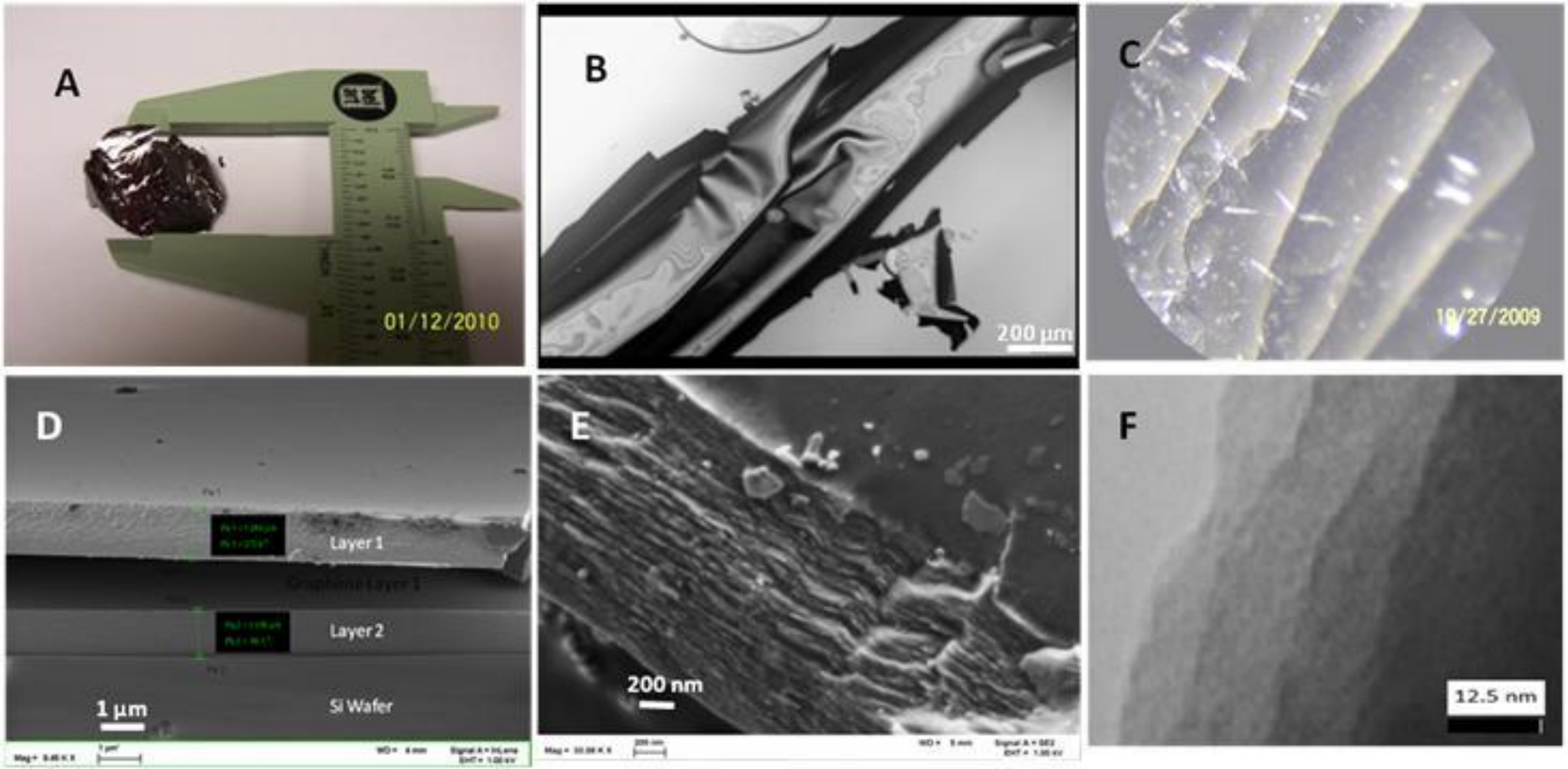


Figure. GUITAR graphene, **A –** a photograph of a flake approximately 25 mm in diameter. **B –** an optical micrograph (400x) in water. **C –** graphene layers (400x). **D –** 9.45K x SEM of microtomed layers on Si. **E –** 23.08K x SEM showing layered characteristics. **F –** A TEM showing layered characteristics on the nanometer scale.

Synthesis of GUITAR

- **Controlled combustion at 900 ^{0}C**
  - Organics MP - BP between 100 to 250 ^{0}C
  - Elemental or Organic Sulfur

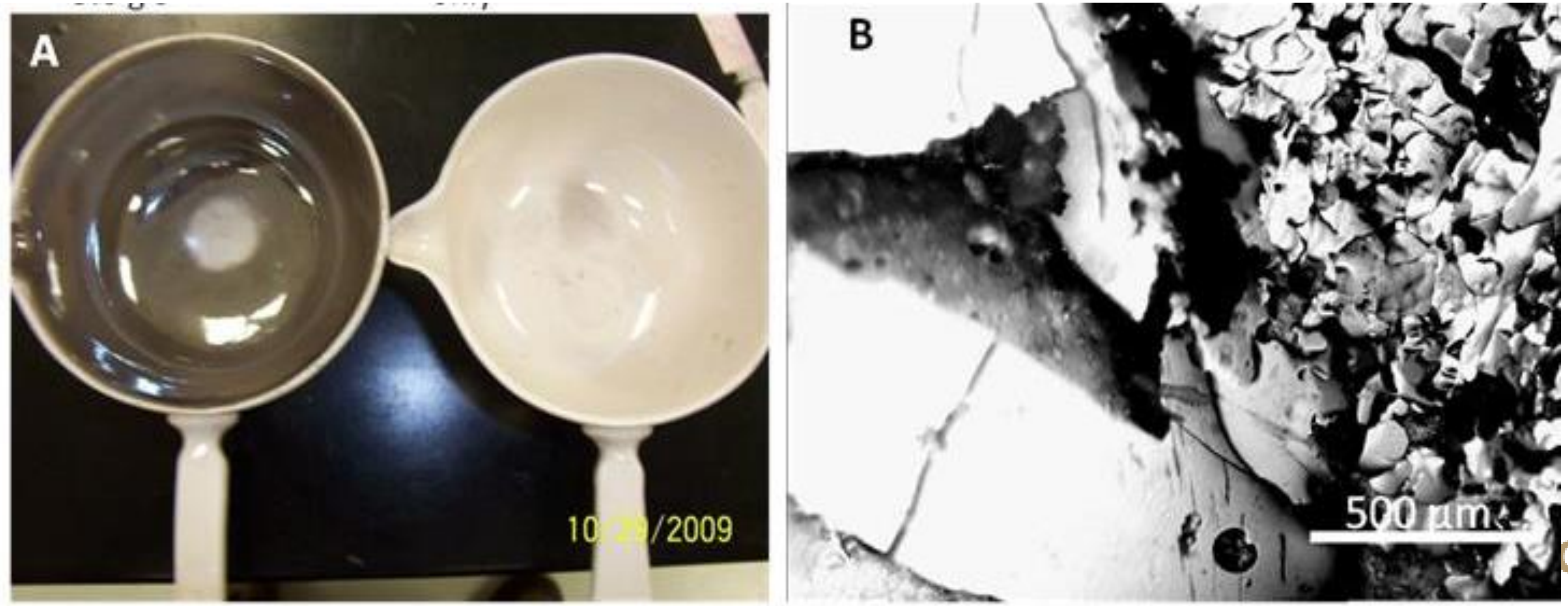
- **Successful Reagents (contains S)**
  - Shale Oil
  - Crude Oil
  - Roofing Tar (Ace Hardware)
  - Taco Chips
  - Some Candy Bars

- **Failed (S free)**
  - Motor Oil, 5W-20
  - Paraffin
  - Pyrene

Mechanism of Formation

- Hunch – Sulfur is Involved

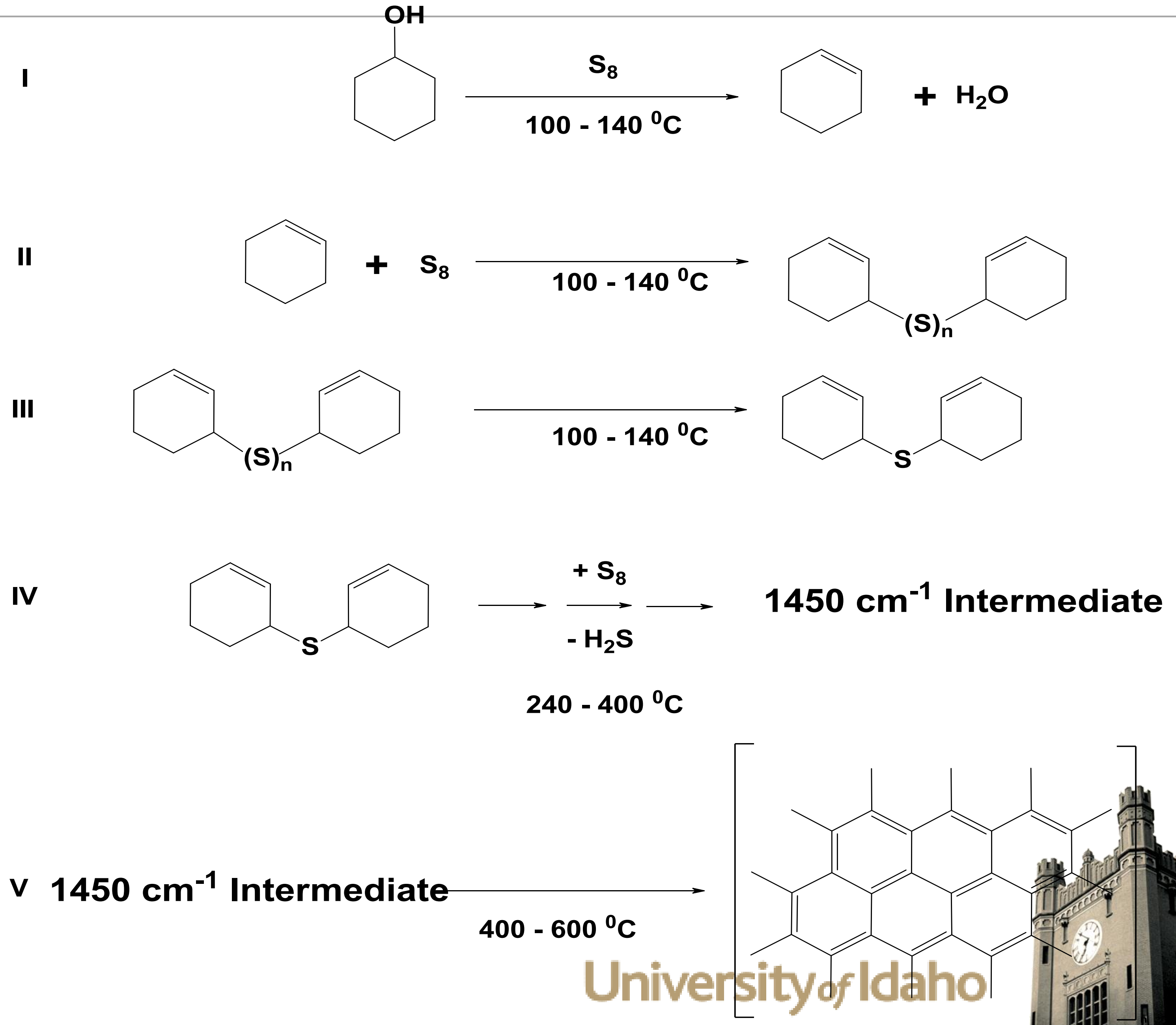
cyclohexanol and Sulfur **cyclohexanol only**



Hypothesized TAR Mechanism

Cheng et al, *J. Mater. Chem*. 2012, **22**, 5723

- 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

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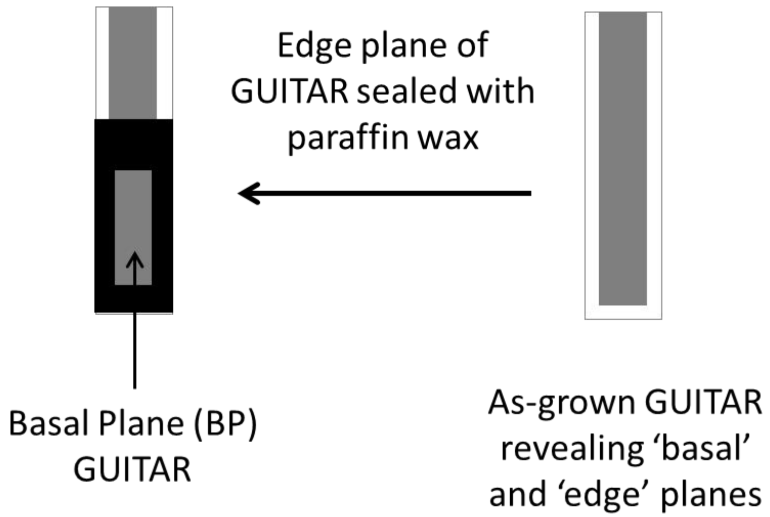
GUITAR electrode fabrication

- Vapor deposit GUITAR onto silicon wafer @ 900 ^{0}C
- Transfer the GUITAR flakes onto mica by vacuum grease or 3M double sided conductive tape



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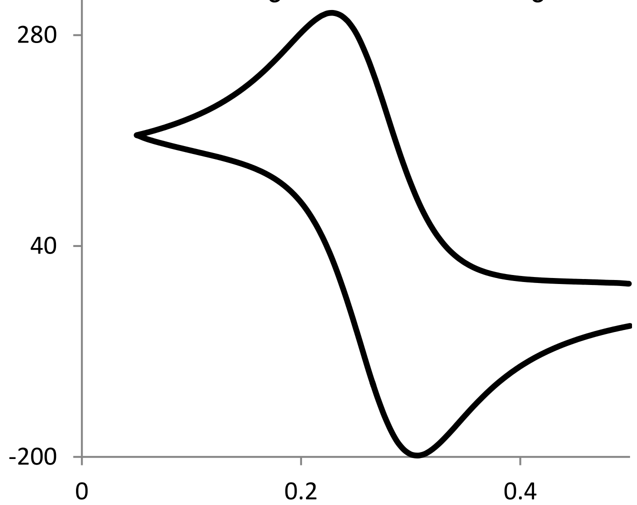
Cyclic Voltammetry Indicates that GUITAR has excellent e- transfer rates with dissolved redox couples.

1 cm², 0.1 M KCl(aq) at 50 mV/s.

ΔE_p = 73 ± 5 mV

n = 3

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



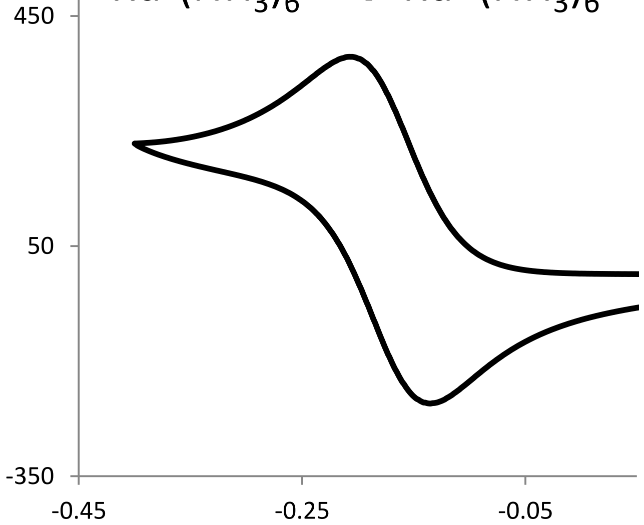
$Fe^{III}(CN)_6^{3-}$ + e- → $Fe^{II}(CN)_6^{4-}$

Ferricyanide

μA/cm²

E (V) vs Ag/AgCl

$Ru^{II}(NH_3)_6^{2+}$ ← $Ru^{III}(NH_3)_6^{3+}$ + e-



$Ru^{III}(NH_3)_6^{3+}$ + e- → $Ru^{II}(NH_3)_6^{2+}$

Ruthenium Hexamine

ΔE_p = 69 ± 1 mV

n = 3

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Graphene and HOPG are poor electrodes

- Calculated Standard Rate Constant (k^0) for GUITAR

$Ox + ne^- \rightleftharpoons Red$ k^0 (cm/s)

	$Fe(CN)_6^{3-/4-}$	$Ru(NH_3)_6^{3+/2+}$	
GUITAR	**1.2×10^{-2}**	**1.7×10^{-2}**	This Work
HOPG	10^{-9} to 10^{-6}	10^{-5} to 10^{-3}	Literature
Graphene	10^{-10} to 10^{-9}	2.5×10^{-3} to 5×10^{-3}	

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Why is GUITAR a superior electrode?

- Density of Electronic States (DOS)
- Low DOS near Fermi Level for crystalline graphites
  - HOPG
  - Graphene
- Next Slide

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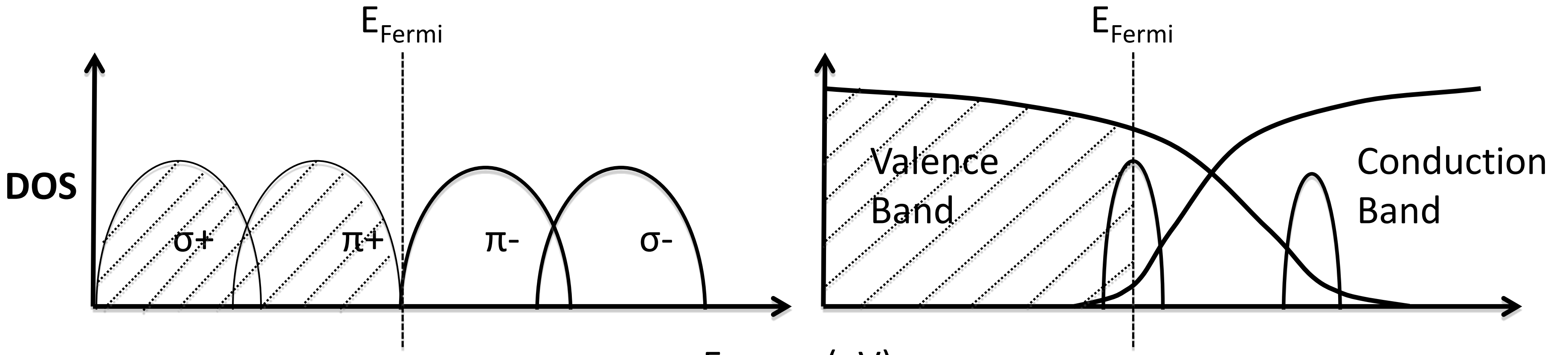
McCreery et al, J. Phys. Chem. 1994, 98, 5314-5319



Energy (eV)

Crystalline Graphite

Disordered Graphite

From McCreery Table 5

	Free e- density (cm^{-3})	DOS at Fermi Level states/atom/eV
Au	6×10^{22}	0.28
HOPG	5×10^{18}	2.2×10^{-3}

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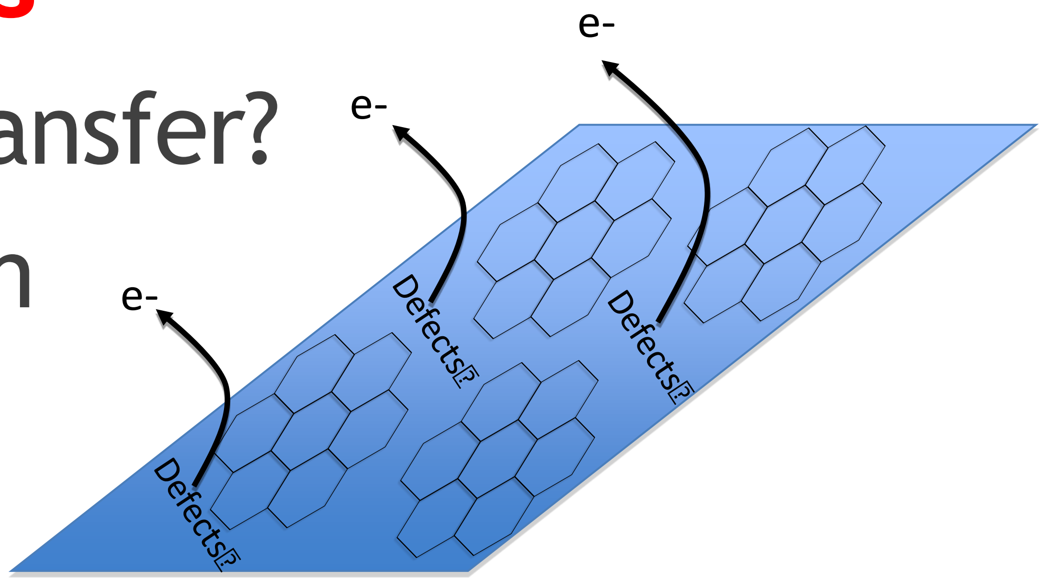
GUITAR Electrodes

- **Higher DOS along Structural Defects?**
- **Structural Defects**
  - Sites for fast e- transfer?
  - Nano-crystals 5 nm



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Aqueous Potential Window

- Positive (anodic) Limit
  - Corrosion, for carbon electrodes:

    $C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$ $E^0 = 0.207$ V
  - Water: $2H_2O \rightarrow O_2 + 4H^+ + 4e-$ $E^0 = 1.23$ volts

- Negative (cathodic) Limit:
  - Water: $4H^+ + 4e^- \rightarrow 2H_2$ $E^0 = 0.00$ volts

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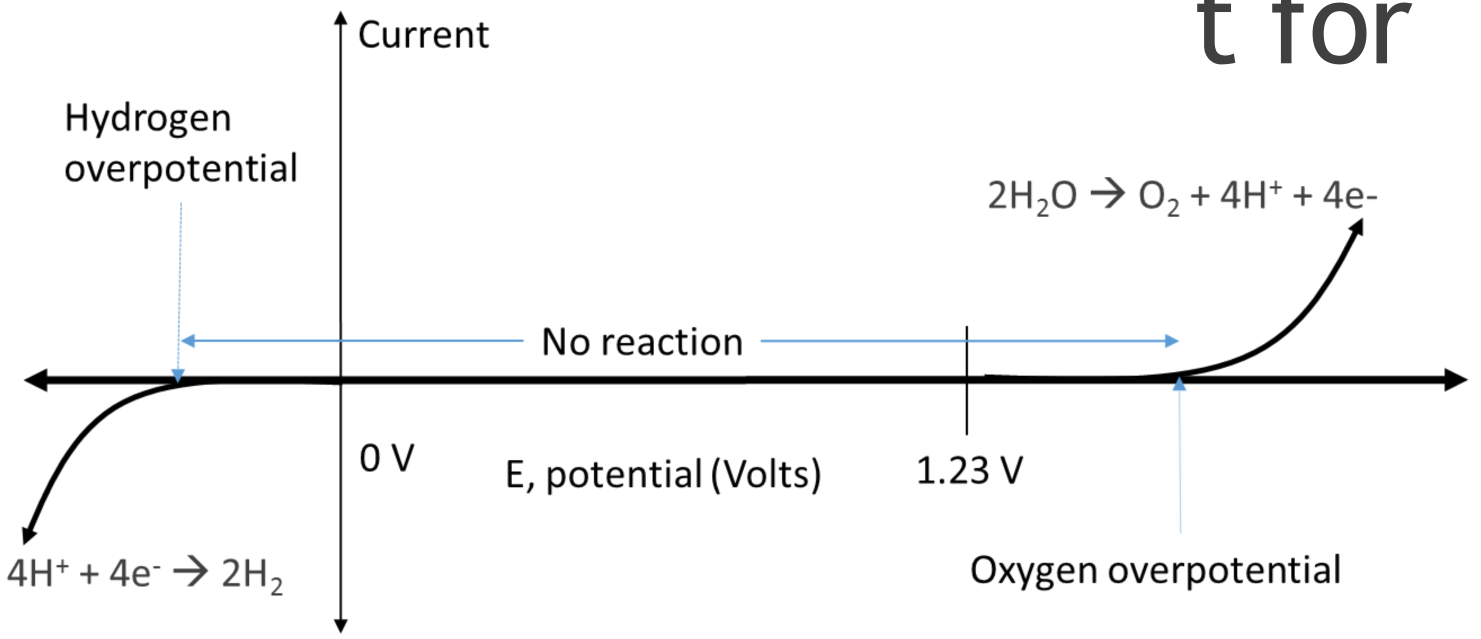
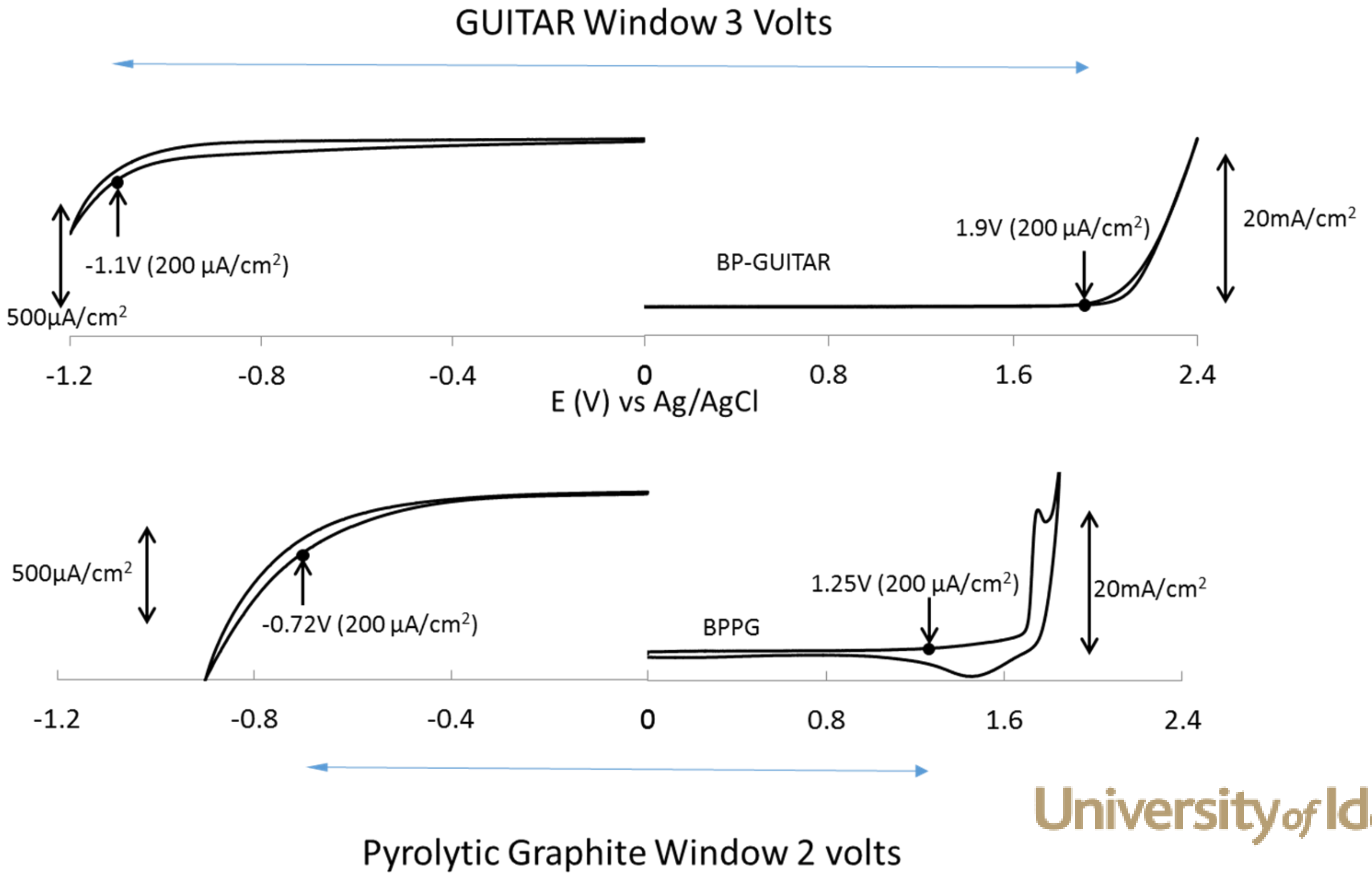
Aqueous Potential Window – Voltammetric Characteristics

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



Potential Windows in 1 M H_2SO_4



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Summary of Potential Windows in 1 M H_2SO_4

Material	Cathodic limits (V)	Anodic limits (V)	Total Windows (V)	Current Limits (μA/cm²)	Reference
GUITAR	**-0.9**	**2.1**	**3.0**	**200**	**This work**
Graphites†	*-0.4 – -0.5*	*1.4 – 1.9*	1.9 – 2.3	200	This work & Literature
Synthetic Diamonds‡	*-0.4 – -1.25*	*1.7 – 2.4*	2.3 – 3.5	200 – 300	Literature

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

‡ Synthetic Diamonds include; boron doped diamond, low and high sp^2 diamond and diamond-like-carbon.

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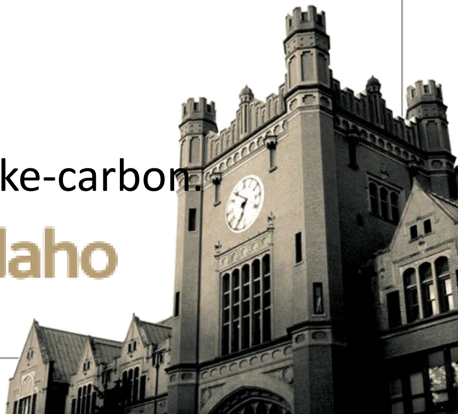

GUITAR Aqueous Potential Window

- 3 V in other Electrolytes, e.g. H_3PO_4, KNO_3, $HClO_4$, Na_2SO_4
- 3 V is Competitive with Synthetic Diamond Electrodes
- Surpasses the 2 V Windows of other Graphitic Materials
  - Glassy Carbon
  - Graphite
  - HOPG
  - Graphene

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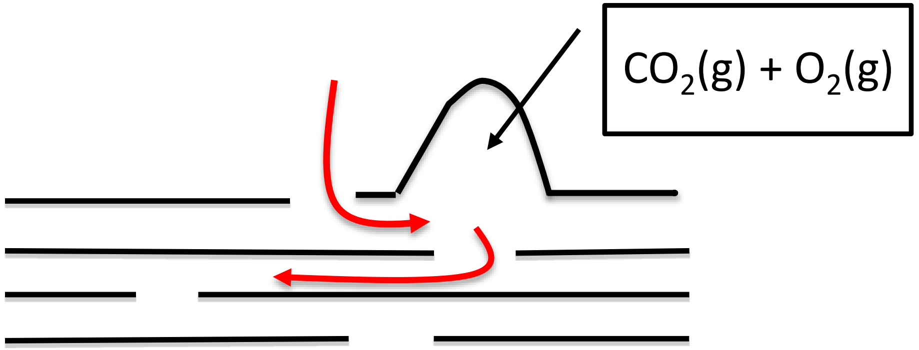
Why Does GUITAR Have a Large Potential Window?

- Cathodic Limits – Hypotheses are being developed

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

- Described by Murray et al, *Analytical Chemistry*, **1993**, *65*, 1378 & **1995**, 67, 2201

Blister formation on graphitic anodes



Gas Evolution, Blister and Pit Formation

- Forward voltammetric scan
  - 2 gas evolution reactions:
    - $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$
    - $C + 2H_2O = CO_2 + 4H^+ + 4e^-$
  - Electrolyte intercalation:
    - $[C_x] + [HSO_4^-] + y\ H_2O = [C_x^+\ HSO_4^-]y(H_2O) + e^-$
- Reverse scan
  - Electrolyte de-intercalation
    - $[C_x^+\ HSO_4^-]y(H_2O) + e^- = [C_x] + [HSO_4^-] + y\ H_2O$

Murray et al, Analytical Chemistry, 1995, 67, 2201-2206

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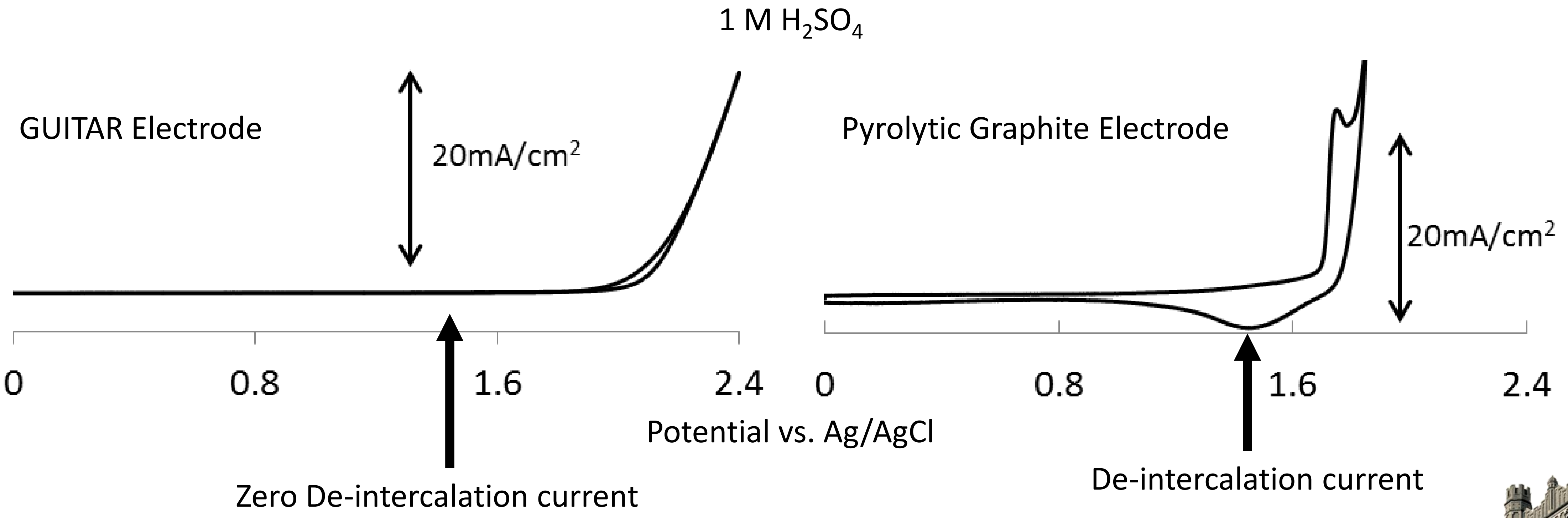
GUITAR Lacks Voltammetric Evidence for Electrolyte Intercalation



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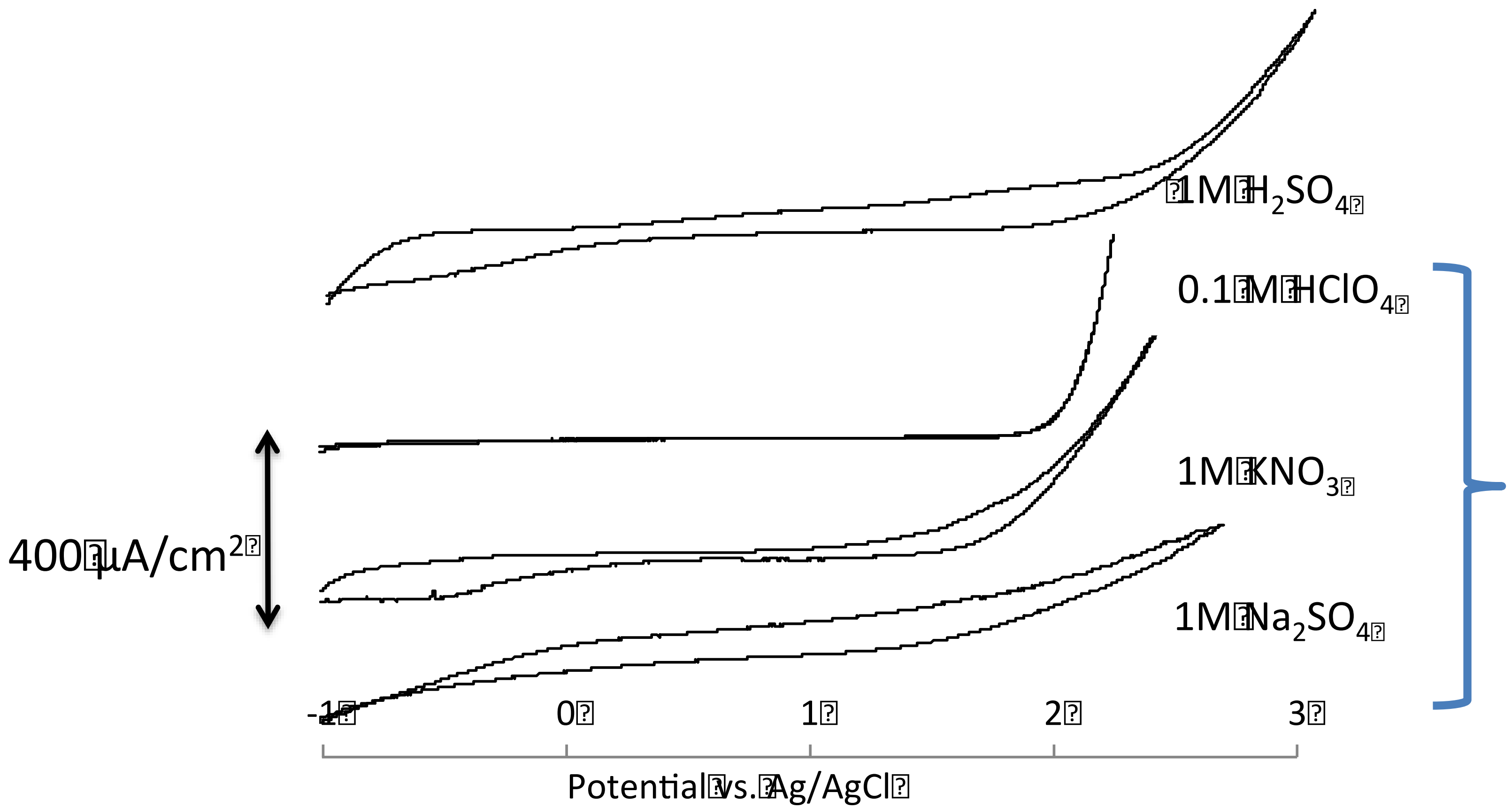
GUITAR anodes do not exhibit electrolytic intercalation



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.

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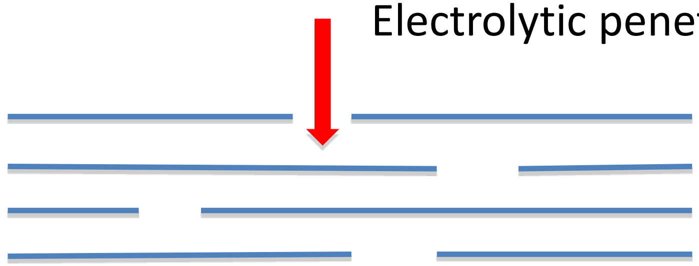
Current Model

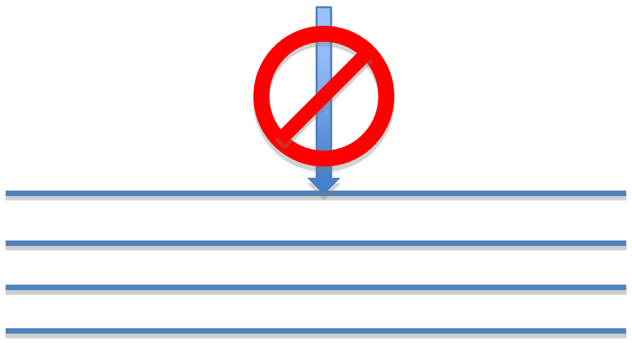
HOPG anodic limit 1.7 V

Electrolytic penetration



Micron size grains
Pin-Holes
-Fewer DOS

GUITAR anodic limit 2.1 V



Nano-size Grains w/Structural Defects
Pin-Hole Free?
-Higher DOS

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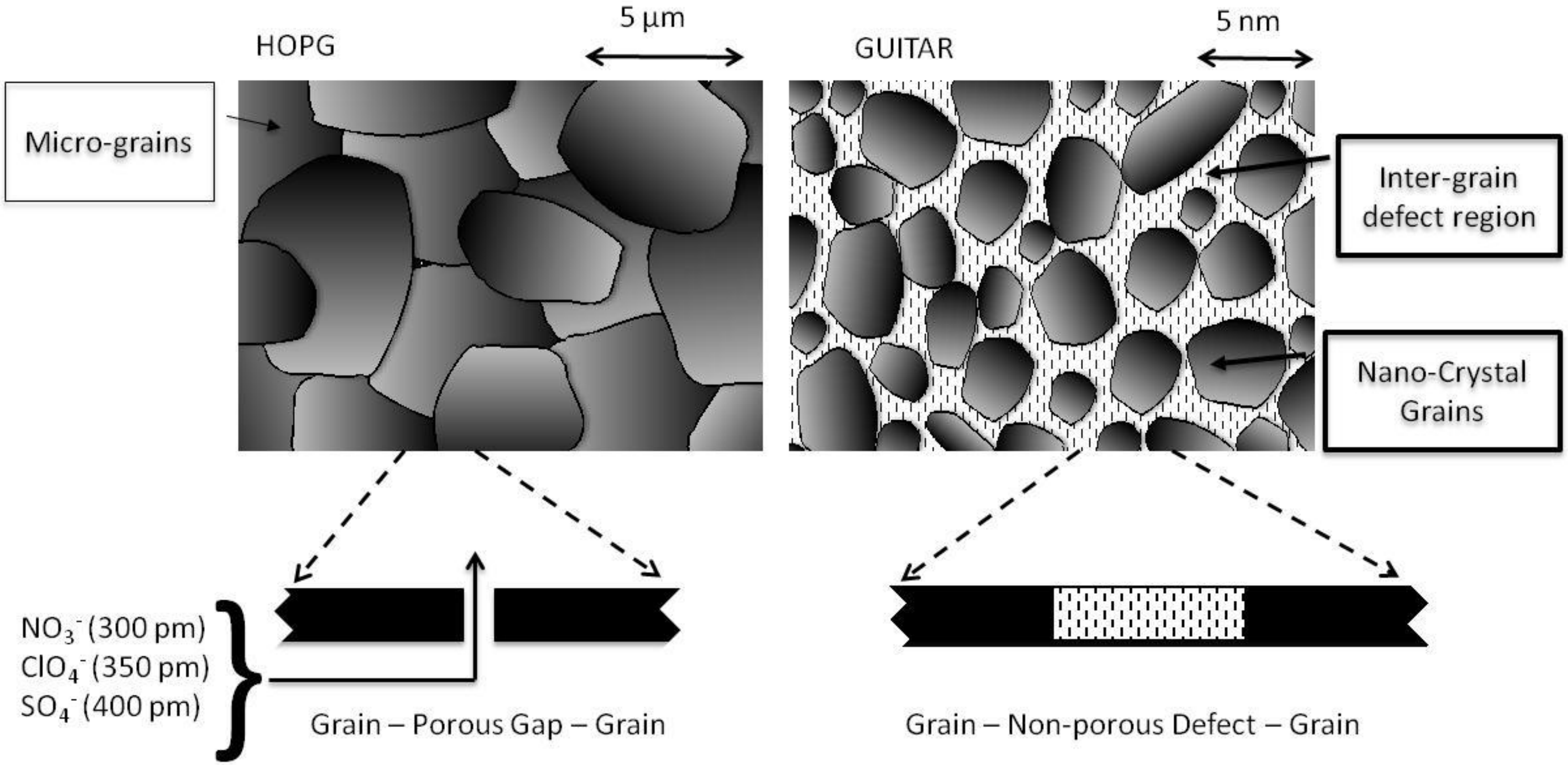

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Ultracapacitors & Energy Storage

- $E = \frac{1}{2} CV^2$
- Energy Storage
  - Increased Capacitance
  - Increase Cell Voltage, V
    - Potential window
  - Aqueous Systems Preferred
    - $H_2SO_4(aq)$
- Requires Zero Faradaic Current
  - Charging or Capacitive only

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Capacitance Studies

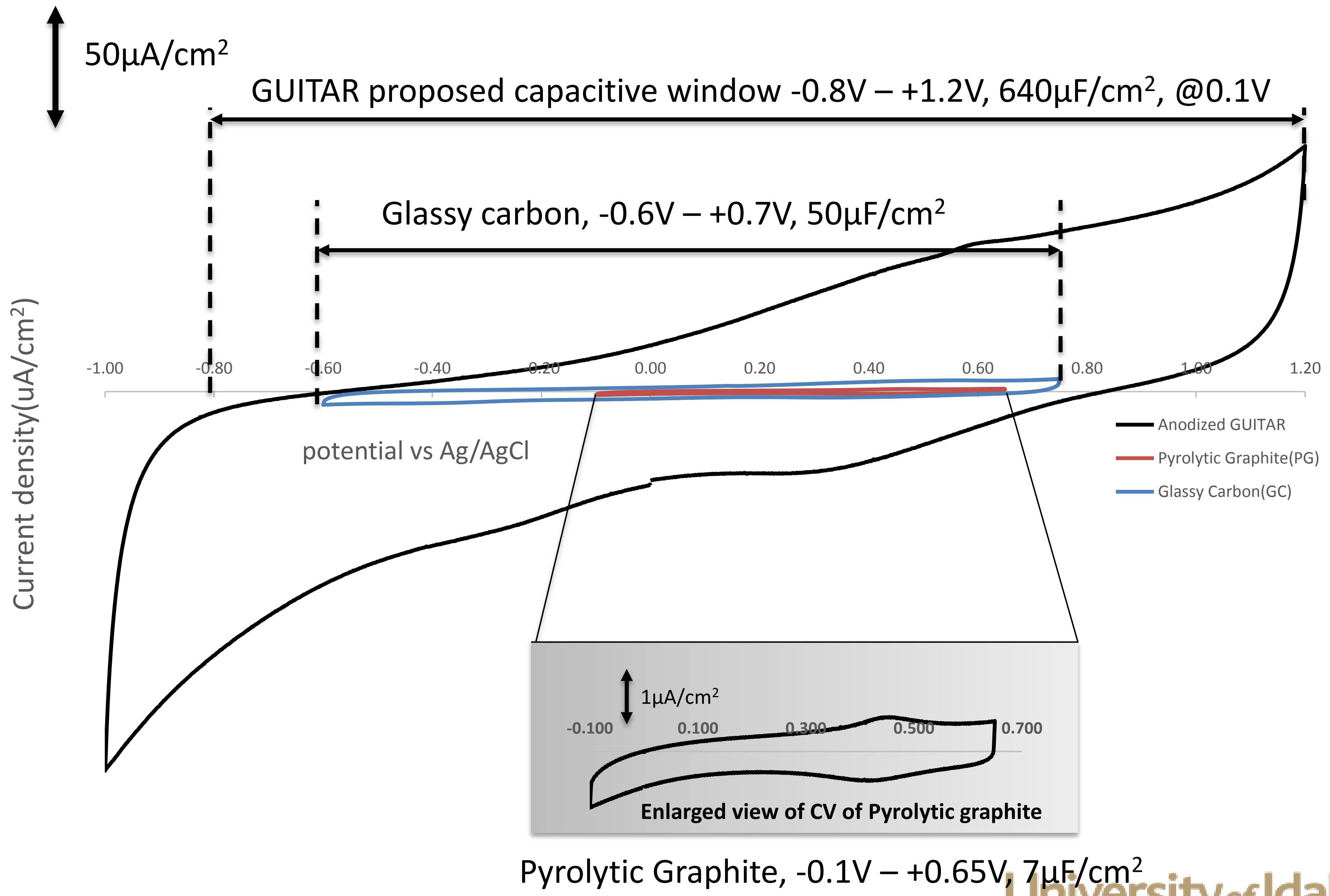
- GUITAR has much higher capacitance than other materials - DOS ?

- Capacitors Applications Require Zero Faradaic current

    - Narrower potential window than 200 μA/cm^2 limits

- Cyclic voltammetric measurements

$$C = \frac{i}{dV/dt}$$



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Material	Cathodic Limit (Volts)	Anodic Limit (Volts)	Capacitive Window (Volts)	Capacitance (μF/cm^2) @ 0.1 V
GUITAR	-0.8	1.2	2	640
Glassy Carbon (Bioanalytical Systems)	-0.6	0.7	1.3	50
Pyrolytic Graphite	-0.1	0.65	0.75	7
Activated Carbon (literature)			0.8 V	10

- GUITAR has more capacitance per unit than other carbon electrodes
- GUITAR has a wider capacitive window than other carbon electrodes

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GUITAR vs. Activated Carbon (AC)

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

- Potential Window, & Capacitance,
  - $C = 10\ \mu F/cm^2$
  - $V = 0.8\ V$

- Expected Performance:

- **AC)** **Energy = $\frac{1}{2} CV^2$ = 3 μJ/cm^2**

- **GUITAR)** **Energy = 1300 μJ/cm^2**

GUITAR vs. Activated Carbon (AC)

- AC surface area ≅ 1000 m^2/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

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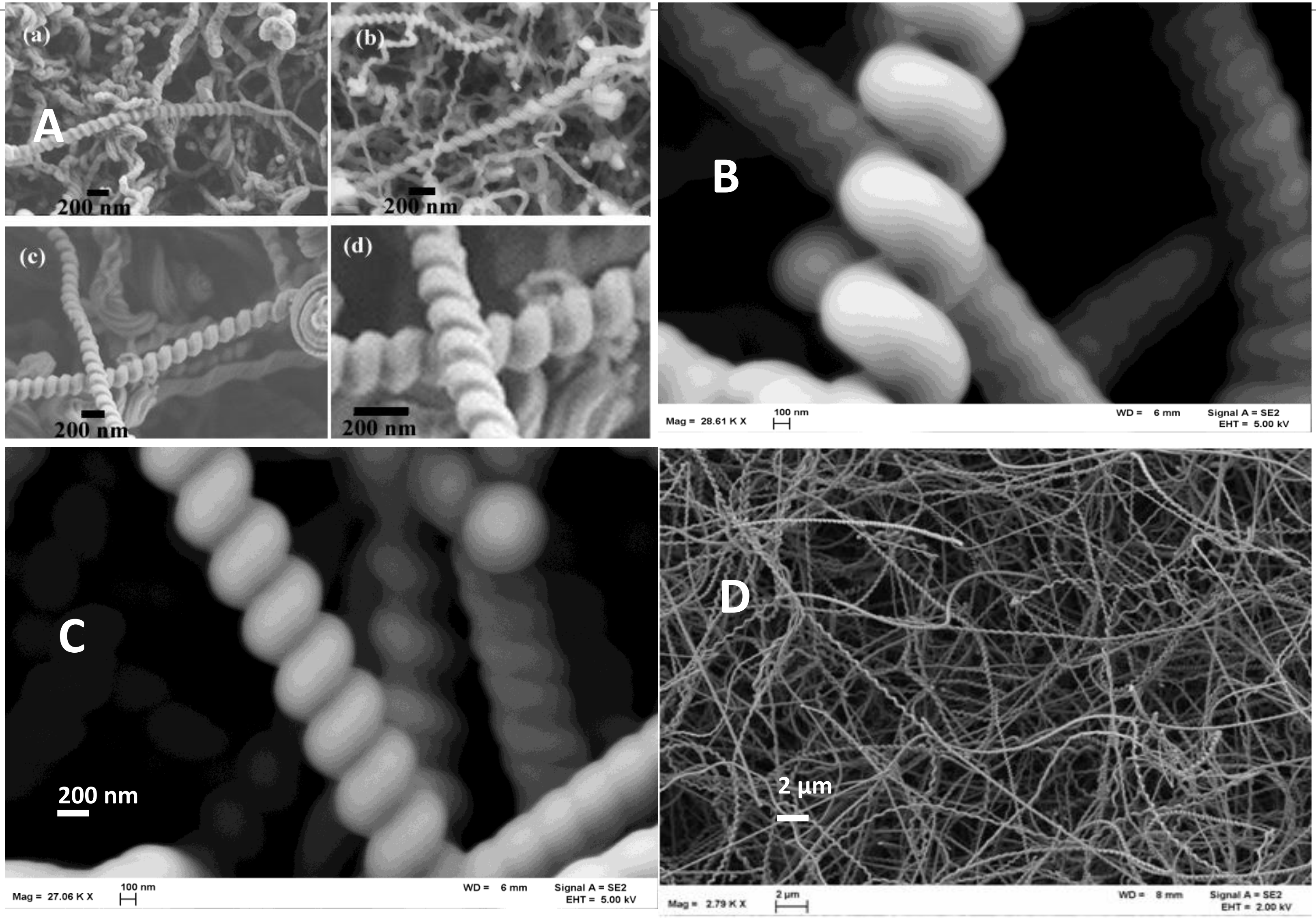

A – Bare silica McIlroy nanosprings. **B – D** Silica nanosprings coated with G-UI-TAR.

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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 H_2 overpotential and, e- transfer kinetics
- **Enhancing Lead-Acid Battery**
  - Requires corrosion resistance, high O_2 and H_2 overpotential, conformal coatings on microporous materials, and electrochemical conductivity.
- **CNT Replacement in Fuel Cells**
  - GUITAR on nanosprings

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END OF PRESENTATION

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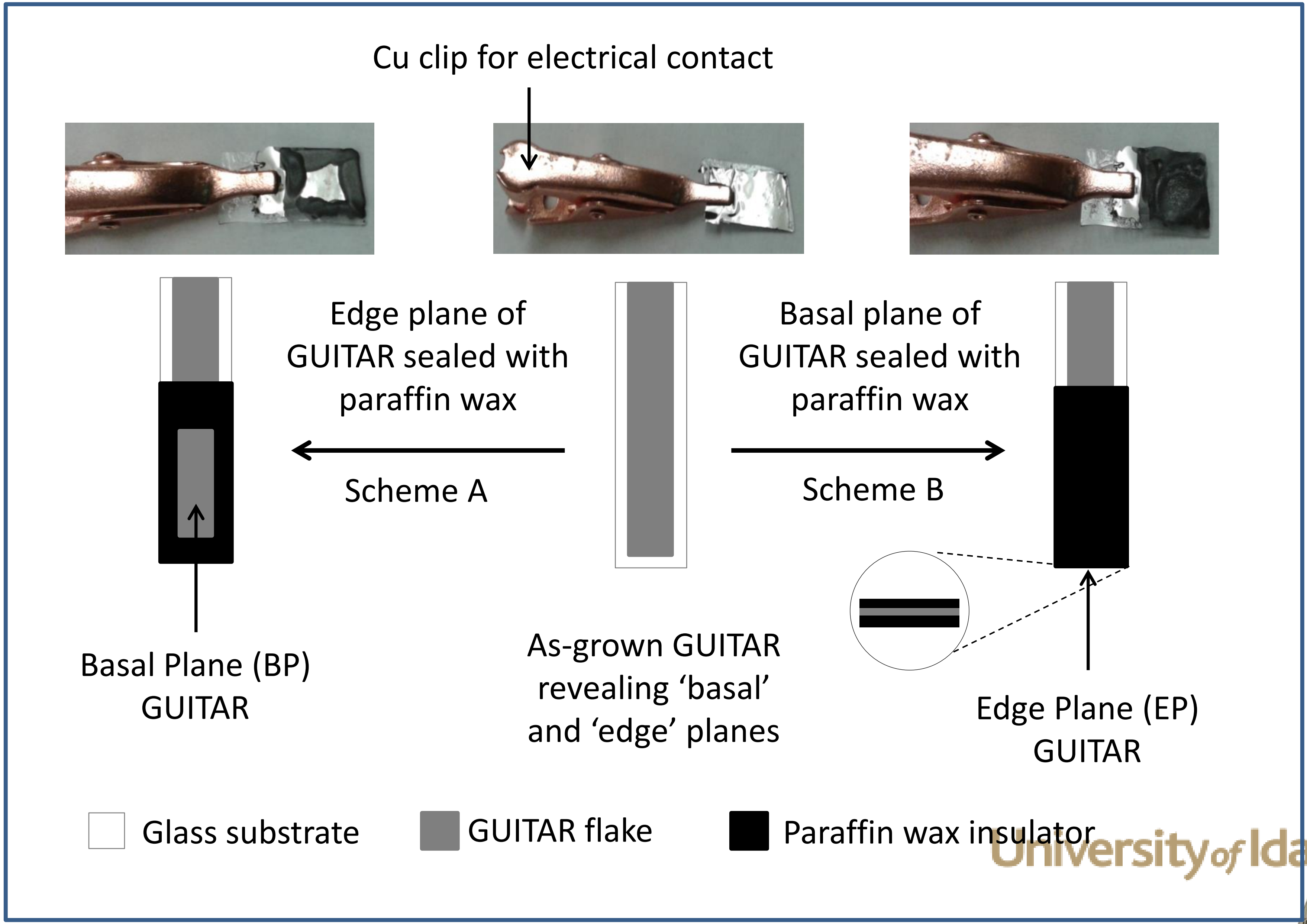
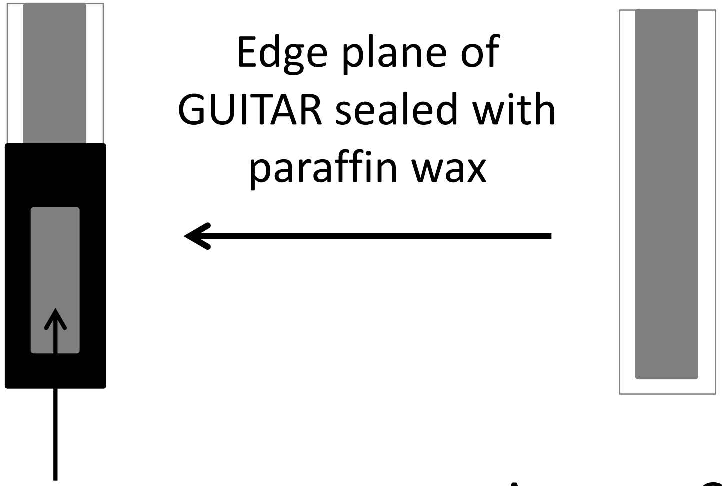
SCRATCH SLIDES

Fig. 2



Cu clip for electrical contact
Edge plane of GUITAR sealed with paraffin wax
Scheme A
Basal plane of GUITAR sealed with paraffin wax
Scheme B
Basal Plane (BP) GUITAR
As-grown GUITAR revealing 'basal' and 'edge' planes
Edge Plane (EP) GUITAR
Glass substrate
GUITAR flake
Paraffin wax insulator



Edge plane of GUITAR sealed with paraffin wax

Basal Plane (BP) GUITAR

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

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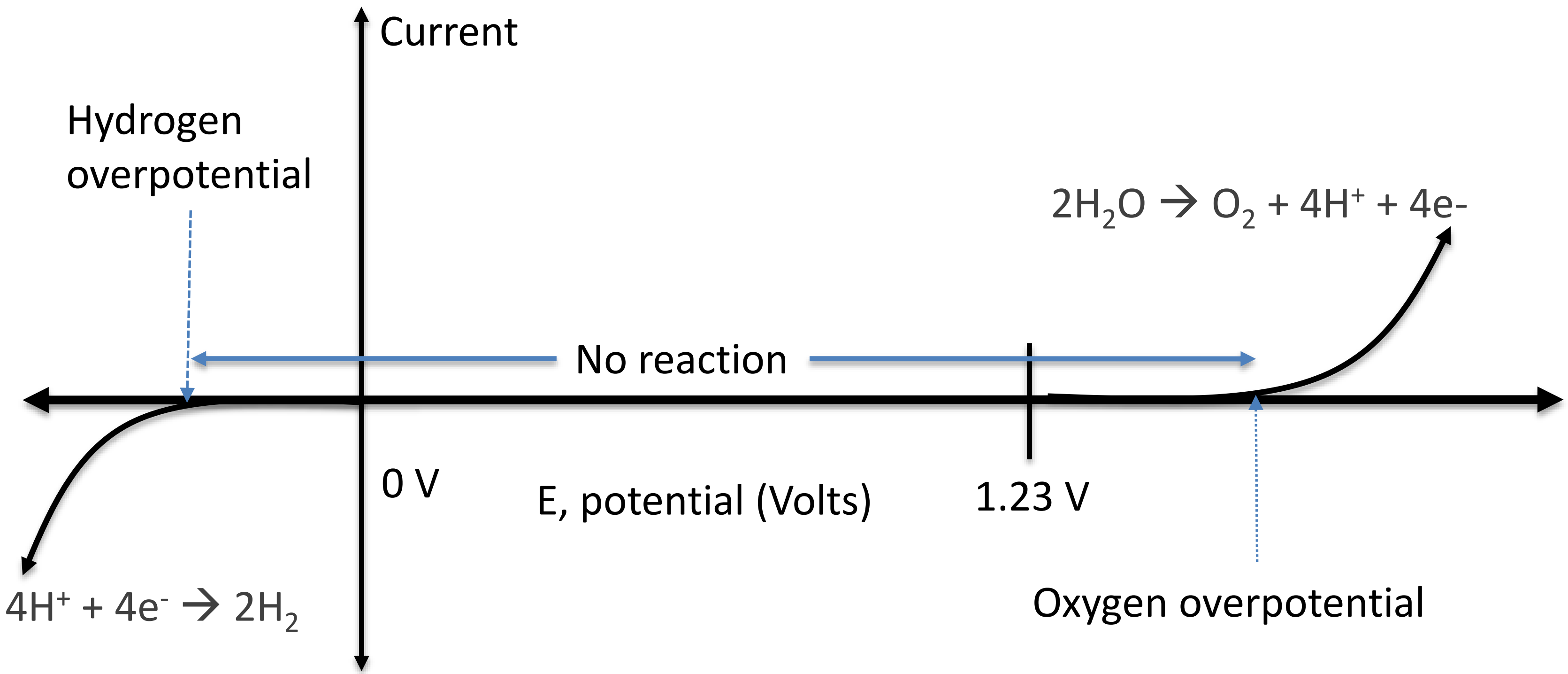

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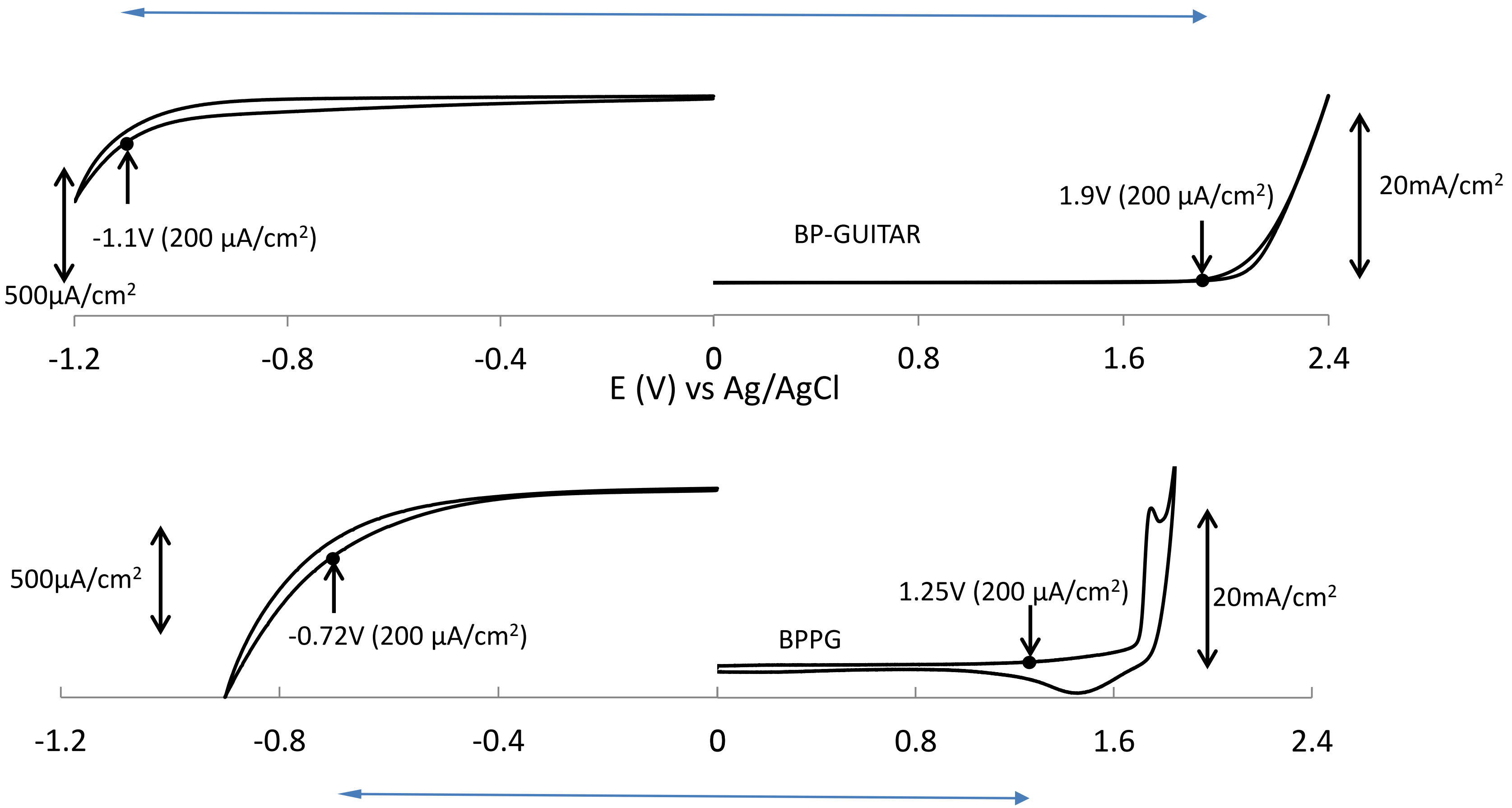
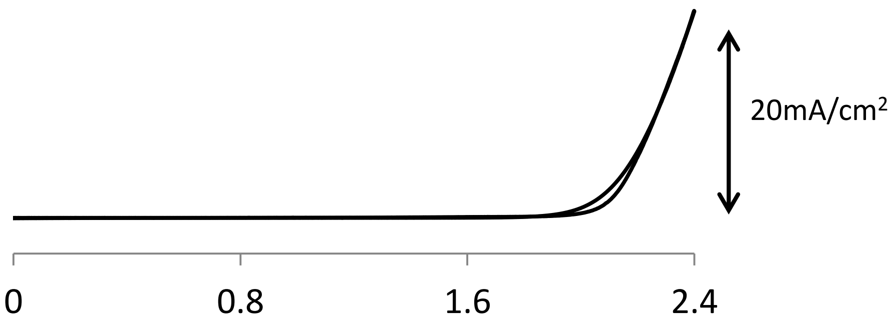
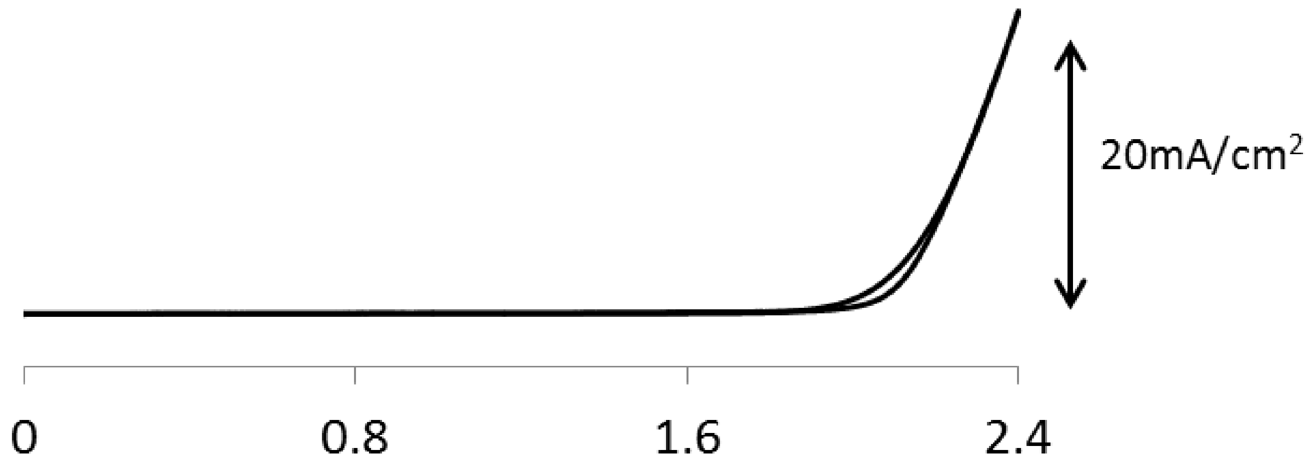
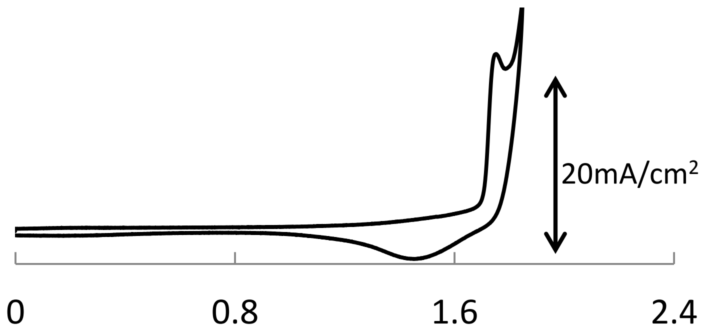
GUITAR Window 3 Volts

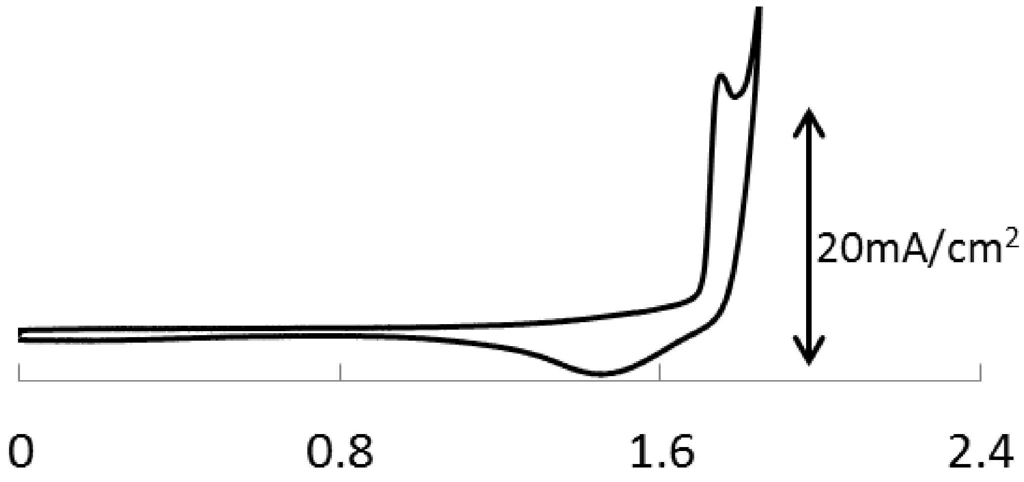


Pyrolytic Graphite Window 2 volts









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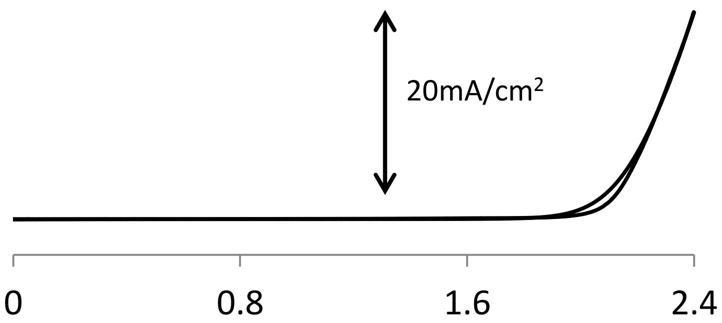
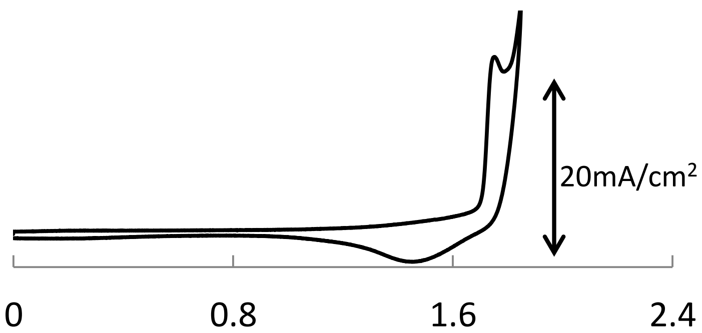

20mA/cm2
0
0.8
1.6
2.4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