Redox Active Polymers for Electrochromism and Charge Storage: Towards Cellulose-Based Substances

John R. Reynolds
School of Chemistry and Biochemistry
School of Materials Science and Engineering
Center for Organic Electronics and Photonics
Georgia Tech Polymer Network

Collaborations with Robert Moon (RBI), Sai Shum (BASF), Mark Losego (MSE)
Flexible Organic Electronics

Displays

Transistors

Energy generation

Electrochromics

Sensors

Siegfried, B. Nature materials 2013, 12 (10), 871.
Electronics on Cellulose Substrates

• Physical Advantages
  – Mechanical properties
  – Biodegradable
  – Combustible
  • Transient electronics

• Processing Advantages
  – Truly abundant
  – Aqueous systems
  – Roll to roll compatible

Challenge of Paper-Based Electronics

• Intrinsic roughness makes solid state device fabrication difficult
• Certain electronic devices benefit from roughness and high surface area
  ➢ Electrochemical devices
  ➢ Electrochromism
  ➢ Charge Storage

Absorptive/transmissive (window type) ECDs

- Residential windows
- Office privacy glass
- Aircraft and automotive windows, sunroofs
- Vision systems (goggles, motorcycle helmets)

Reflective ECDs

- E-ink, e-paper
- Self-dimming mirrors
- Numeric and wearable displays

Siemens AG; Acreo AB; Sage Electrochromics, Inc.; Triton Systems, Inc.; Gentex Corp., LTI Smart Glass, ChromoGenics, Eclipse Energy Systems, Inc
Charge Storage Via Electrochemical Supercapacitors

**High power applications**

- Break regeneration, HEVs, wind turbine pitch control,
- low voltage ride through, energy storage, start-stop systems

**Low power applications**

- Power tools, digital cameras, lighting, PC cards, RFIDs,
- server backups, camera flash, wireless sensor networks
If Molecular and Polymer Syntheses are the Enabling Science ... 

Molecular Design and Computation
Macromolecular/Assembly Design
**Molecule and Polymer Synthesis**

Redox Chemistry
Optoelectronic Properties
Energy Level Matching
**Processability:**
- BHJ → Spin/Blade and Slot-Die solution coating
- DSSC → Surface adsorption
- Electrochromics → Spraying

Then Processing and Control of Morphology are the Controlling Factors for Success...
Spanning the Visible Spectrum

Redox activity in conjugated polymers

Neutral Polymer

Radical Cation

Dication
Hitting the Limit With All of the Subtractive Primaries

What is the processing gap?

Spin Coating

Blade Coating

Slot Die Coating

Roll to Roll

Limitations:
- Inefficient materials use
- Not roll to roll compatible

http://www.tciinc.com/Capabilities.aspx
Solution Processable Conjugated polymers for Organic Electronics and Energy Applications

**Advantages:** Many soluble polymers already developed (we understand much of the synthetic chemistry) and several coating methods are available in our laboratory.

**Challenges:** controlled/optimal morphology, scale of synthesis, environmentally benign solvent processing

**Opportunities:** morphology and material properties to mimic commercial coating processes... large-scale, high-throughput fabrication
Diffuse Reflective ECDs

- Diffuse white electrolyte
- No color-matching needed
- Same ECP used at working and counter electrode

White Diffuse Reflecting Gel Electrolyte

% Reflectance

Wavelength (nm)
Reflective Device Switching—Movies

Magenta—1 sec switch

Magenta—0.25 sec switch
Color Control Via Solution Mixing

Solution Blends

Film Blends Prepared by Spray Processing

Cyan + Magenta  Magenta + Yellow  Cyan + Yellow

25:75  50:50  75:25
Tuning To Black in Solution Blended ECPs
Cyan-Periwinkle 2-Magenta 2-Yellow 2 (C-P$_e$ 1-M 2-Y 2)

- Color neutral
- More broadly absorbing
- Transmissive oxidized state

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>%$T_{550}$ Neutral</th>
<th>%$T_{550}$ Oxidized</th>
<th>$\Delta %T_{550}$</th>
<th>%$T_{\text{int}}$ Neutral</th>
<th>%$T_{\text{int}}$ Oxidized</th>
<th>$\Delta %T_{\text{int}}$</th>
<th>(L*$^<em>$,a</em>$^<em>$,b</em>$^*$) Neutral</th>
<th>(L*$^<em>$,a</em>$^<em>$,b</em>$^*$) Oxidized</th>
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<tr>
<td>C-P$_e$ 2-M 2-Y 2</td>
<td>582</td>
<td>10</td>
<td>61</td>
<td>51</td>
<td>11</td>
<td>57</td>
<td>46</td>
<td>38, 0, -5</td>
<td>82, -3, -4</td>
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</table>

*Integration Range is 430-730 nm. 3-1.3-1-1 w/w mixture
Nanocellulose Based Electrodes and Electrochromics

- Advantages of nanocellulose
  - High transmittance with low sheet resistance demonstrated (CNT, AgNWs)
  - Mechanically robust

CNF Transparent Electrode

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<tr>
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<th>No SWNTs</th>
<th>290 Ω/sq</th>
<th>73 Ω/sq</th>
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<td>(a)</td>
<td></td>
<td></td>
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<tr>
<td>(b)</td>
<td></td>
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</tr>
<tr>
<td>(c)</td>
<td>290 Ω/□ &amp;</td>
<td>90 % @ 550 nm</td>
<td>73 Ω/□ &amp;</td>
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<tr>
<td></td>
<td></td>
<td>81 % @ 550 nm</td>
<td>81 % @</td>
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PEDOT:PSS EC Device

WO₃ EC Device

Window Type Electrochromic Devices
Switchable Glasses via Blade Coating

- 1.0 V
Intermediate
+ 1.0 V

Switching time approx. 1 sec
Path Forward: Electrochromic Polymers on Cellulose

**Key Challenge:** Creating conductive cellulose-based electrodes that remain color neutral.

**Approach:** Surface confined polymerization with functionalized monomers to generate a conductive coating of cellulose fibrils.
Electroactive Polymer (EAP) Based Electrochemical Supercapacitors

Device weight: ca. 0.5 g

Type I PXDOT device architecture
Solution processed supercapacitors
Redox-active polymers + nanocellulose

Cladaphora Nanocellulose
Flexible PEDOT-Paper

Layer by Layer coating of active materials

CNF Aerogel
PEDOT:PSS
poly[2-(3-thienyl)ethoxy-4-butyl- sulfonate]
SWCNT

Expanding the Voltage Window and Capacitance with ProDOT$_x$-EDOT$_y$ Co-Polymers

Increasing the amount of EDOT lowers the oxidation potential and extends the voltage window.

Effect of EDOT Content on Type I Device Fill Factor

Increasing EDOT content → broader electroactive window → higher fill factor
Carbon Nanotube Substrates as Conducting Scaffolds for Soluble PXDOT-based Polymers

3 www.rsc.org/chemistryworld/2012/06/challenging-consensus-nanotube-electrochemistry
Switching to the solvent resistant PE$_2$ resulted in a **2x increase in the mass capacitance**, **5.5x increase in areal capacitance**, and a scan rate dependence that is linear up to 200 mV/s ($t_{\text{dis}}: 4$ sec). Incorporations of PE$_2$ slows down discharge rate but devices still exhibit **highly symmetrical charge/discharge curves**.
Devices encapsulated between PET showed complete retention of capacitance with a bending radius as low as 0.6 mm.

Preliminary bending tests show that the device capacitance is not compromised even after 300 cycles.
Going Green and Going Fast: Water Soluble and Solvent Resistant ProDOT$_x$-EDOT$_y$ Co-Polymers
Why Aqueous Processable and Compatible Materials?

1. **Environmental issues and biocompatibility:**
   Films of water soluble polymers can be fabricated with minimal environment impact in a variety of processing locations. Replacement of toxic and/or flammable organic solvent with water allows for safer fabrication and operation of these materials in devices.

2. **Faster charge/discharge rates**
   From our PXDOT electrochromic research we know that high affinity to aqueous electrolytes leads to faster ion diffusion processes and switching speeds.

OS-ProDOT-EDOT can be synthesized using direct arylation polymerization in excellent yields (94%).
WS-ProDOT-EDOT readily dissolves in H₂O at 4mg/mL and can be coated using roll-to-roll compatible methods (such as spray coating) onto the substrate of choice.
Protonation of WS-ProDOT-EDOT using dilute acid yielded a solvent resistant polymer film (SR-ProDOT-EDOT) that is stable to both organic and aqueous systems!
Aqueous Type I devices incorporating solvent resistant PE
Highly stable supercapacitors

Maintains a linear scan rate dependence up to 10 V/s
Film capacitance @ 50 mV/s: 48.2 ± 2.5 F/g
Film capacitance @ 2 V/s: 35.8 ± 1.5 F/g

0.5 M NaCl-H$_2$O or 0.5 M LiBTI-H$_2$O

100 mS charge/discharge time over 1 volt window

Maintains > 75 % of initial capacitance after 175k cycles at 1 V/sec.
Device assembled in air with NaCl/H$_2$O electrolyte.
Perspective

• Conjugated polymers many different roles in energy modulation, harvesting, conversion and storage.

• Direct arylation polymerization is scalable for appropriate pi conjugated polymers for electrochromism and charge storage

• Electron rich dioxyheterocycles find utility in electrochromism and charge storage where cellulose based substrates can be effective

• We need to consider the scalability of the synthesis and the process as we design new active polymers for cellulose substrate based devices

• Water processable conjugated polyelectrolytes bring possibilities of environmentally compatible aqueous processing for charge storage…. and electrochromism…. and beyond?
Thank You
Device Encapsulation

- Device fabrication inside glovebox
- Two ECDs:
  - Inside chamber (50°C and 80% relative humidity)
  - On benchtop
- Little change in initial and final transmittance contrast after 40 days

Kim, Kim, Graham, Dyer, and Reynolds
*Solar Energy Materials & Solar Cells* 2012, 100, 120–125
Films sprayed in air, enclosed under **argon**, exposed in weatherometer 24 hours.

Films sprayed in air, enclosed under **air**, exposed in weatherometer 24 hours.
ECP-Black Device with ~50%DT
9 square inch ECP-Black Device Memory

Dual-polymer Device
- High contrast ECP at working electrode
- Minimal coloring ECP at counter electrode
- ITO/glass electrodes
- Transparent gel electrolyte

- Initial 5 min at +2V (bleached) or -2V (colored)
- Open circuit for 15 min.
- 5 sec refresh pulse to +/- 2V
- Open circuit again

% Transmittance

Wavelength

400 450 500 550 600 650 700

61.4% T

12.1% T

% Transmittance

Minutes

0 10 20 30 40 50 60 70 80 90 100

Open circuit 15 min
5 sec refresh pulse