New Materials & Printing Methods for Printed Polymer Electronics

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Outline

1. Challenges in printed electronics

2. Enabling materials

3. Printed demonstrator circuits


Lodge, Science **2008**, 321, 50.
Printing Circuits

Use direct write methods to print circuits onto paper or plastic substrates

Printing Methods –

- Flexographic
- Offset
- Gravure
- Ink Jet
- Aerosol Jet
- Screen

Roll-to-Roll (R2R) Sheet-to-Sheet

Functional Inks – metals, semiconductors, insulators

- Metal colloids
- Polymer semiconductors
- Polymer insulators

Plextronics Semiconducting Ink
Science and Technology of Organic Semiconductors

Applications

New applications in OLEDs, displays, lighting, solar cells, sensors, photodetectors, OFETs, printed circuitry, optically pumped lasers

Older applications in xerography, photography

- \(\pi\)-electron rich, van der Waals solids
- Processable at low temperature
- Absorb, emit in the visible
- Carrier mobility \(10^{-3} \text{ – } 10 \text{ cm}^2/\text{Vs}\)
- Tunable electronic properties

In devices, interfaces are crucial!

Printed electronics

OLED lighting

Sony OLED TV
Operating Speeds in Applications

- Pressure sensor
  - Takao Someya

- E-paper
  - Plastic logic

- Flat panel display
  - Samsung

- RFID tags
  - Avery Dennison

~ 10 Hz  10-100 Hz  100 kHz - 10 MHz
Switching Speed vs Supply Voltage for Printed Electronics

![Graph showing the relationship between supply voltage (V) and delay per stage (s) for printed electronics. The x-axis represents supply voltage ranging from 1 to 100 volts, while the y-axis represents delay per stage ranging from $10^{-6}$ to $10^0$ seconds. Various symbols and lines are used to represent different data points, indicating the dependence of delay on supply voltage.]
Need Low Voltages, Focus on Dielectric

Thin Film Transistor

\[ C = A\varepsilon\varepsilon_0 / t \]

How do we boost capacitance?

- Smaller \( t \)
  
  Nanodielectrics (ultra thin)

- Bigger \( \varepsilon \)
  
  \( \text{HfO}_2, \text{SrTiO}_3, \text{electrolytes} \)

\( \text{current } \propto \text{charge concentration } \times \text{speed} \)

\[ I_D = \frac{W}{L} C(V_G - V_T) \mu V_D \quad \text{for } V_D \ll V_G \]
**Polymer Electrolytes: Printable, High Capacitance Gates**

*Boost the charge density in the OTFT channel, lower operating voltage*

Idea: Use polymer/salt mixtures commonly used in batteries, fuel cells, capacitors, ...

**Example:** polyethylene oxide (PEO)/LiClO$_4$

Large degree of polarization = Large capacitance (~10-100 μF/cm$^2$)
Comparison of $\text{SiO}_2$ and Electrolyte Capacitors

“traditional” inorganic dielectric
(ex. 150 nm $\text{SiO}_2$)

- polarization of atomic clouds
- $Q' = C'V$
- $C' = \frac{k \varepsilon}{t}$ ($t =$ dielectric thickness)
- $Q'_{\text{max}} \sim 10^{13}$ charges/cm$^2$
- $V \sim 150$ V

$\sim 10$ nF/cm$^2$

mobile ion-based electrolyte dielectric
(ex. PEO + LiClO$_4$)

- macroscopic migration of ions
- double layer formation, $Q' = C'V$
- $C' = \frac{k \varepsilon}{\lambda}$ ($\lambda =$ Debye length)
- $Q'_{\text{max}} \sim 10^{15}$ charges/cm$^2$
- $V \sim 3$ V

$\sim 10$ $\mu$F/cm$^2$
Concept: Electrolyte-Gated OTFT
A Typical Ionic Liquid

Physical Property Data

- Melting point: -18 °C
- Density: 1.52 g/cm³
- Viscosity: 32.6 cP
- Electrical conductivity: 9.1 mS/cm
- Vapor pressure (RT): <10⁻⁷ torr

**Ion Gels**

**Ion gel:** ionic liquid + polymer network

Self assembly of ABA triblock copolymer:

Poly(styrene-**b**-methyl methacrylate-**b**-styrene) \(\text{SMS}\)

Poly(styrene-**b**-ethylene oxide-**b**-styrene) \(\text{SOS}\)

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide \([\text{EMI}]\text{[TFSI]}\]

Transparent, Rubbery Ion Gel

Ion Gel (Ionic Liquid + Polymer Network)
Printing using a Dense Aerosol Jet

Ultrasonic Atomizer (pictured):
- 0.7 ~ 10 cP ink handling viscosity

Pneumatic Atomizer (also available):
- 1 ~ 2500 cP ink handling viscosity

Nozzle Output:
- Small Aerosol Droplets ~ 1 – 5 µm
- Up to 0.25 microliter/sec dispensing speed
- < 5 µm line width printing capability to > 1 mm

Various Nozzle Sizes for Line Width Control

Fine Line Capability
- 10 micron line width, 30 micron pitch

Dr. Mike Renn
All-Printed GEL-OTFT

Gate Contact: PEDOT:PSS in water (Baytron P)

Dielectric: 90 wt% ethyl acetate
9.5 wt% [EMIM][TFSI] (Solvent Innovation)
0.5 wt% PS-PMMA-PS

Semiconductor: 0.5 wt% PQT in chloroform (American Dye Source)
5% Terphenol added

S/D Contacts: Au nanoparticle ink (UT Dots)
xylene (or PEDOT:PSS)

Substrate: Kapton or PEN (Dupont)
Semi-Transparent TFTs with PEDOT:PSS Electrodes

- For electrical contacts:
- Au is too expensive...
- Ag can react with ion gel...
- Can use PEDOT:PSS

Ink Formulation:
90 wt% PEDOT:PSS (Baytron P)
10 wt% Ethylene glycol

Printed Thickness: ~500 nm
Conductivity: ~500 S/cm
**Top-Gated All-Printed GEL-OTFT**

Drain Current (A) vs. Gate Voltage (V)

- $V_D = -1 \text{ V}$
- $W/L \sim 20$

- Forward
- Reverse

![Image of a top-gated OTFT device](image)

Drain Current (A) vs. Drain Voltage (V)

- $V_D = -1.75 \text{ V}$
- $V_D = -1.50 \text{ V}$
- $V_D = -1.25 \text{ V}$
- $V_D = 0.00 \text{ V}$

PEDOT:PSS
Ion gel
PQT12
Au
Polyimide substrate

*Nature Materials, 2008*
Operating Gel-Gated Transistor
transfer curves with various drain voltages

Characteristics of Printed P3HT TFTs
Stability (Tested in Air)

V_D = -1 V

1 day

V_D = -1 V

1 month

Drain current (A)

Gate voltage (V)
Resistor-Loaded Top-Gated Inverter

- **Input Electrode:** PEDOT:PSS (Baytron P)
  - Water

- **Dielectric:** 9.3 wt % [EMIM][TFSI]
  - (Solvent Innovation)
  - 0.7 wt % PS-PMMA-PS
  - 90 wt % Ethyl Acetate

- **Semiconductor:** 3 mg/ml P3HT (Rieke)
  - 90 vol% Chloroform
  - 10 vol% Terpineol

- **Resistor:** Carbon Ink (Asahi)
  - Carbitol Acetate

- **Contacts:** Au nanoparticle ink (UT Dots)
  - Xylene

- **Substrate:** Kapton or PEN (Dupont)

![Diagram of the Resistor-Loaded Top-Gated Inverter with labeled components and connections.](image)
Resistor-Loaded Top-Gated Inverter

![Diagram of a resistor-loaded top-gated inverter](image)

- **Input Voltage (V)**
- **Output Voltage (V)**

**Gain**

- $V_{DD} = -1.5V$

**Graph**

- **V$_{OUT}$ (V)**
- **Input Voltage (V)**

- **Forward**
- **Reverse**
Five-Stage Ring Oscillator

Delay Time
\[ t = \frac{1}{2Nf} \]
\[ \sim 1 \text{ ms} \]

Adv. Funct. Mater., 2010

V_{BIAS} \quad V_{DD}

T_{L1} \quad T_{L2} \quad T_{L} \quad T_{L4} \quad T_{L5} \quad T_{L6}

T_{D1} \quad T_{D2} \quad T_{D3} \quad T_{D} \quad T_{D5} \quad T_{D6}

V_{out}

V_{BIAS} = -2V \quad V_{BIAS} = -2.25V \quad f \sim 150 \text{ Hz}

V_{OUT} (V)

Time (ms)
NAND Logic Gate (200 Hz)

<table>
<thead>
<tr>
<th>$V_A$</th>
<th>$V_B$</th>
<th>$V_{OUT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

V_A (100 Hz)  
V_B (200 Hz)  

$V_{OUT}$  
$V_{DD} = -1V$

Input Voltage (V)  
Output Voltage (V)

Time (ms)  
Adv. Funct. Mater., 2010
Single Wall Carbon Nanotubes

**Pure Tubes: Ultra-High-Purity SWNTs**
- SWNT purity: ~99%
- SWNT diameter range: ~1.2 - 1.6 nm
- Delivery: aqueous solution
- Price: contact for quote

_Nanointegris, Inc. (Skokie, IL)_
Ion Gel Gated CNTs TFT: Ambipolar Transport

Ambipolar TFT: both holes and electrons can be transport in the semiconductor layer.

\[ I_D = \frac{W}{L} C(V_G - V_T) \mu V_D \] (\(C \sim 1/d\))
Printed Ion Gel Gated CNT Thin Film Transistors

Ambipolar Transistor: 50 µm × 500 µm

- \( \mu: \sim 50 \text{ cm}^2/\text{Vs} \)
- \( I_{\text{ON}}/I_{\text{OFF}}: 10^3 \sim 10^5 \)
- \( V_{\text{th}}: 0.5 \sim 0.8 \text{ V} \)

High output current, low operation voltage
Printed Ion Gel Gated CNT TFT and Inverter

TFT

- W/L = 10
- Ion Gel
- PEDOT:PSS
- G
- S
- D
- 300 µm
- Ion Gel
- 20 nm
- 1 µm
- 0 nm

μ ~ 10-50 cm²/Vs
I_{ON}/I_{OFF} ~ 10^{3}-10^{5}
V_{th} ~ 0.5 – 0.8 V
>98% Semiconducting CNT

Inverter

- GND
- V_{in}
- V_{DD}
- n
- p
- V_{out}

<table>
<thead>
<tr>
<th>V_{in}</th>
<th>V_{out}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

V_{DD} = 1.5V

Voltage (V)

- 1 kHz
- Polyimide

0.0 0.5 1.0 1.5
0.8 1.0 1.2 1.4

Time (ms)

0 1 2 3 4
Stage delay time of a ring oscillator is determined by RC time constant of the each stage.

$$t = (R_{Channel} + R_{Gate} + R_{Gel}) \times (C_{channel} + C_{parasitic})$$

When $R_{Channel}$ and $C_{Channel}$ are dominant in system,

$$t = R_{Channel} \times C_{channel} = \frac{V_{DD} C_{channel}}{I_{channel}}$$

$$t \approx \frac{V_{DD} C_i WL}{\mu C_i \frac{W}{L} V_{DD}^2} = \frac{L^2}{\mu V_{DD}}$$

(ideal situation)

With 50μm channel, mobility =10cm²/Vs, $V_{DD}$=2V, the delay time is:

$$t \approx \frac{(50 \times 10^{-4}) cm^2}{10 cm^2 / Vs \times 2V} = 1.25 \mu s$$
22 kHz, 5-Stage CNT Ring Oscillator

Delay Time, \( t = \frac{1}{2N_f} = 5 \mu s \) !!
Printed Driving Circuit of a Flexible Display

Function:
switch a printed electrochromic display.
tunable frequency.
low voltage operation.

Key Elements:
Electrolyte-gated OTFT;
Electrolyte-gated capacitor;
Electrolyte-gated electrochromic display.

20 OTFTs

15 Capacitors

Display

20 Resistors

10 Crossovers

1 cm
Output Pulses of Printed Circuit

without load display

with load 6 mm² display pixel

Voltage (V)

Time (s)

PEDOT:PS

Ion Gel

Semiconductor

Metallic CNT

Voltage (V)

Time (s)

-1

0

no display

1 mm² display

2 mm² display

6 mm² display
Dynamic Output Characteristics of Circuit

The output performance of a complete printed circuit with pixel. The circuit is measured in air for more than 10 times.
Changes of the Absorption Spectrum of Printed Pixel

Abs (normalized)

Wavelength (nm)

V=1.5V
V=0V
V=-1V

PEDOT:PSS

Electrolyte

Semiconductor
MCNT

PEDOT:PSS

Electrolyte

Semiconductor
MCNT
Dynamic response of a stand-alone printed pixel, driven by 0.25Hz input 1V voltage. 525nm, P3HT absorption peak; 855nm, PEDOT:PSS absorption peak. Time resolution is about 0.4s.
The operational stability of printed circuit over 100 minutes. Measured in N₂, without display pixel.
**Summary**

**Electrolyte Gates provide:**
- Low voltage (< 2 V)
- **Printable**
- 200 kHz operation (5 µs)
- New transistor architectures
- Physics at high carrier densities

**Next Challenges**
- Develop truly complementary inverters
- Increase circuit speed
To produce high-density circuits on flexible substrates based on liquid phase coating, printing and patterning operations carried out in an engineered R2R sequence

$7.5 Million over 5 years
1. Challenges in printed electronics

2. Ion gels: a new class of polymer electrolytes

3. Applications of ion gels as printable, high capacitance materials for printed circuits


Potential Dependence of the Conductivity of Highly Oxidized Polythiophenes, Polypyrroles, and Polyaniline: Finite Windows of High Conductivity

David Offer, Richard M. Crooks, and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received April 6, 1990

*Two microelectrodes, called source and drain, are connected with a conducting polymer and a small fixed potential, $V_D$, is maintained between them. At the same time, their potential vs a reference electrode, $V_G$, is varied, thus changing the state of charge of the polymer and therefore its conductivity. When the polymer is conducting, significant drain current, $I_D$, flows between the source and the drain, but when the polymer is insulating negligible drain current flows. $I_D$ is directly proportional to the conductivity of the polymer. Thus, a plot of $I_D$ vs $V_G$ gives relative conductivity vs potential.
Reproducibility (100 transistors)

- **Mobility**
  \[ \mu_{\text{air}} = 2.0 \pm 0.7 \text{ cm}^2/\text{Vs} \]
  \[ \mu_{\text{vac}} = 2.1 \pm 0.7 \text{ cm}^2/\text{Vs} \]

- **ON/OFF ratio**
  \[ r_{\text{air}} = 1.1 (\pm 0.7) \times 10^5 \]
  \[ r_{\text{vac}} = 1.6 (\pm 1.3) \times 10^5 \]

- **Turn on voltage**
  \[ V_{\text{air}} = 0.5 \pm 0.1 \text{ V} \]
  \[ V_{\text{vac}} = 0.2 \pm 0.1 \text{ V} \]

**D Flip-Flop Circuit with Reset Function (5 Hz)**

D flip-flop with Reset function
8 NAND gates + 3 Inverters

**Timing Parameter**

<table>
<thead>
<tr>
<th>Timing Parameter</th>
<th>Output Data Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>“0” to “1”</td>
</tr>
<tr>
<td>$T_{C-Q}$</td>
<td>35ms</td>
</tr>
<tr>
<td>$T_{SETUP}$</td>
<td>10ms</td>
</tr>
</tbody>
</table>

**Graph:**

- **Input Voltage (V):**
  - D flip-flop with Reset function
  - 8 NAND gates + 3 Inverters

- **Output Voltage (V):**
  - CLK (5Hz)
  - Data (2.5Hz)
  - $V_{DD} = -1.5V$

**Graph Details:**

- **Time (s):**
  - 0 to 1
- **Output Voltage (V):**
  - -1.5 to 0

**Graph Values:**

- **CLK (5Hz):**
  - Data (2.5Hz):
Inverter Stability (in vacuum)

$V_{DD} = -1.5V$

Output Voltage (V) vs. Time (ms)

$V_{ON} - V_{OFF}$ vs. Number of cycles ($\times 10^6$)

- 0 hr
- 6 hrs
- 2 hrs
- 8 hrs
- 4 hrs
Estimation of Parasitic Capacitance

Voltage (V)

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>0.0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>0.0</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ V_{DD} = 2.5V \text{ polyimide} \]

\[ t_{delay} = 50 \mu s = \ln 2 \times RC_{total} \]

delay time per stage depends on total capacitance of one stage.

\[ Q_A = C_p V_{OUT} \]

\[ Q_B = (C_p + C_p + C_c) \Delta V \]

C\(_c\) (channel) \(~1.3\ nF\)

C\(_p\) (parasitic) \(~4.5\ nF\)

C\(_{total}\) (total) \(~5.8\ nF\)

R (averagre of channel) \(~12\ k\Omega\)

Parasitic capacitance is about 22% of total capacitance.

Overshooting peak relates to coupling between ion gel and source and drain electrodes.
Printable, Flexible Electronics
Switching Delay vs Supply Voltage for Printed Electronics

- Switching Delay vs Supply Voltage
- Supply Voltage (V) vs Delay per stage (s)
- Logarithmic scale for both axes
- Data points for different materials: SiO₂, polyimide
Ionic Gel = Ionic Liquid + Polymer Network

Ionic Liquids

\[ \text{[EMIM][TFSI]} \]

\[ \sigma = 7.6 \text{ mS/cm} \]

Triblock copolymer

PS-PMMA-PS

C < C*  

C > C*

\[ \begin{array}{c}
\text{Liquid} \\
\text{Gel} \\
\text{Obstruction Theory prediction}
\end{array} \]

\[ \begin{array}{c}
\sigma (\text{S/cm}) \\
0.10 \\
0.08 \\
0.06 \\
0.04 \\
0.02 \\
0.00
\end{array} \]

**Temperature Effect on Capacitance of Spin-coated Ion Gel**

- **Arrhenius equation**

  \[ C = A e^{-E_a/RT} \]
  
  \[ A = 277.8, \ E_a = 8008 \text{ J/mol (83 meV)} \]

- **Restore its capacitance value upon heating**

- [EMIM] [TFSI] is frozen at around 220 K
Comparison with Circuit Models

50 wt% SOS, 50 °C

RC series circuit:

$$\sigma^* = l / \{A[R+i(\omega C)^{-1}]\}$$

$$\sigma = \sigma' \text{ (high f plateau)}$$
$$C = 1/(\omega R) \text{ (at } \sigma'' \text{ maxima)}$$
$$\tau_{RC} = RC$$

RCPE series circuit:

$$\sigma^* = l / \{A[R+Q(i\omega)^{(-1-\alpha)}]\}$$

$$\sigma = \sigma' \text{ (high f plateau)}$$
$$C = (R^\alpha/Q)^{1/(1-\alpha)}$$
$$\tau_{RC} = RC$$

RC: $C = 3.06 \ \mu F$

RCPE: $\alpha = 0.183; \ Q = 5.47 \times 10^4 \text{ ohm/s}^{0.817}; \ C = 2.59 \ \mu F$

**Materials – Polymer Synthesis**

**SOS**

\[
\begin{align*}
\text{HO}_{(n)}\text{O}_{(n)}\text{OH} & \xrightarrow{(\text{COCl})_2} \text{C}_{12}\text{H}_{25}\text{S} \text{S} \text{O} \text{C} \text{O} \text{S} \text{S} \text{C}_{12}\text{H}_{25} \\
\text{C}_{12}\text{H}_{25}\text{S} \text{S} \text{O} \text{C} \text{O} \text{S} & \xrightarrow{140 \degree C} \text{C}_{12}\text{H}_{25}\text{S} \text{S} \text{O} \text{C} \text{O} \text{S} \text{C}_{12}\text{H}_{25}
\end{align*}
\]

*He and Lodge, Macromolecules, 41, 167 (2008)*

**SMS**

\[
\begin{align*}
\text{EtO}_{\text{Br}}\text{O}_{\text{Br}}\text{Br} & \xrightarrow{\text{PMDETA, CuBr, CuBr}_2, 60 \degree C} \text{EtO} \text{O} \text{Et} \xrightarrow{\text{dNbpy, CuBr/CuBr}_2, 100 \degree C} \text{EtO} \text{O} \text{Et}
\end{align*}
\]


*Patten et al. Science, 272, 866 (1996)*

*Matyjaszewski and Xia, Macromolecules, 30, 7697 (1997)*

### Materials – Polymer Characterization

<table>
<thead>
<tr>
<th>polymer</th>
<th>code</th>
<th>$M_{n, \text{PS}}$ (kDa)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$M_{n, \text{PMMA}}$ (kDa)</th>
<th>$M_{n, \text{PEO}}$ (kDa)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA (initiator)</td>
<td></td>
<td>86</td>
<td></td>
<td></td>
<td>1.20</td>
</tr>
<tr>
<td>PS-PMMA-PS</td>
<td>SMS</td>
<td>17.5</td>
<td>86</td>
<td></td>
<td>1.21</td>
</tr>
<tr>
<td>PMMA&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td>126</td>
<td></td>
<td></td>
<td>1.07</td>
</tr>
<tr>
<td>PEG (initiator)</td>
<td></td>
<td></td>
<td></td>
<td>35</td>
<td>1.04</td>
</tr>
<tr>
<td>PS-PEO-PS</td>
<td>SOS</td>
<td>2.8</td>
<td></td>
<td>35</td>
<td>1.03</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined from $^1$H-NMR.

<sup>b</sup> Synthesized by Dr. Ilan Zeroni using anionic polymerization.*

---

Temperature Effect on Gel Capacitance

\[ C = A \exp \left( -\frac{E_a}{RT} \right) \]

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>A (µF/cm²)</th>
<th>( E_a ) (kJ/mol)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>265</td>
<td>8.2</td>
<td>0.987</td>
</tr>
<tr>
<td>13.4</td>
<td>600</td>
<td>10.0</td>
<td>0.994</td>
</tr>
</tbody>
</table>

- Activation energy: comparable to Hydrogen bonding

- Increased free ion concentration  → Capacitance increase with Temperature
Ionic Conductivity

- Conductivity increases with increasing temperature.
- \( T \) dependence follows VFT eqn.
- Conductivity decreases with increasing polymer concentration.

VFT Fitting Parameters

<table>
<thead>
<tr>
<th>SMS (wt%)</th>
<th>( \sigma_0 ) (mS/cm)</th>
<th>( B ) (K)</th>
<th>( T_0 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>580 ± 20</td>
<td>554 ± 13</td>
<td>165 ± 2</td>
</tr>
<tr>
<td>10</td>
<td>246 ± 15</td>
<td>416 ± 18</td>
<td>189 ± 3</td>
</tr>
<tr>
<td>20</td>
<td>299 ± 29</td>
<td>717 ± 43</td>
<td>161 ± 6</td>
</tr>
<tr>
<td>30</td>
<td>298 ± 21</td>
<td>873 ± 32</td>
<td>164 ± 4</td>
</tr>
<tr>
<td>40</td>
<td>231 ± 7</td>
<td>847 ± 12</td>
<td>184 ± 1</td>
</tr>
<tr>
<td>50</td>
<td>272 ± 6</td>
<td>1045 ± 9</td>
<td>186 ± 8</td>
</tr>
</tbody>
</table>

Vogel-Fulcher-Tamman (VFT):
\[ \sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right) \]

Mackie-Meares Model:

\[
\frac{D_g}{D_0} = \left( \frac{1 - \phi}{1 + \phi} \right)^2
\]

\[D_g\]: diffusion coefficient in gel
\[D_0\]: diffusion coefficient in solvent
\[\phi\]: polymer volume fraction

\[
\frac{\sigma_g}{\sigma_0} = \left( \frac{1 - \phi}{1 + \phi} \right)^2
\]

**Ionic Conductivity**

Rheology and Impedance on the Same Sample

\[ Z = \frac{V}{I} \]
\[ Z^* = Z' - iZ'' \]

Alternatively,
\[ \sigma^* = \sigma' + i\sigma'' \]
\[ \sigma^* = \frac{l}{(AZ^*)} \]
\[ \sigma' = \frac{IZ' \sqrt{(Z'^2 + Z''^2)A}} \]
\[ \sigma'' = \frac{IZ' \sqrt{(Z'^2 + Z''^2)A}} \]

\( A \): area \quad l \): thickness

gap setting

ceramic insulation

stainless steel 25mm parallel plate electrodes

rheological and impedance measurements on the same sample
Ionic Liquids as Electrolytes

Ionic liquids: molten salts with low melting points

- Negligible volatility
- Chemical & thermal stability
- Electrochemical stability
- High ionic conductivity

Electrical Double Layers (EDLs)

\[ C' = \varepsilon_r \varepsilon_0 \frac{1}{d} \]

\[ d \sim 1 \text{ nm} \quad C' > 1 \mu\text{F/cm}^2 \]

The time for ions to establish stable EDLs is an important parameter.
Spin-Coatable Ion Gel Films

1) MIM structure

- Spin coated Ion gel
  SMS+ EMIM TFSI
  Ethyl acetate as a solvent
  Polymer/Ionic liquid = 20 wt%

- Thickness
  Solution concentration
  Spin coating speed

2) Test cell on a glass
Electrical Double Layers and Equivalent Circuit

Electrical double layer

Equivalent circuit (ideally polarizable electrode)

\[ Z' = Z_R + i Z_C \]

\[ Z' = R_{\text{bulk}} + 1/(i\omega C_{\text{DL}}) \]
Impedance Analysis

\[ Z^* = Z' + iZ'' \]

\[ Z^* = R_{\text{bulk}} + \frac{1}{(i\omega C_{\text{DL}})} \]
Thickness Experiments: phase angle vs frequency
**Thickness Dependence of Capacitance, Resistance, & Conductivity**

Average capacitance @ 1 Hz = 12.2 $\mu$F/cm$^2$, @ 10 Hz = 8.4 $\mu$F/cm$^2$

Resistance: linear dependence on thickness

Average conductivity = 0.68 mS/cm
Thickness Dependence of RC time constants

RC time constants: linear dependence with thickness

RC time constants (μsec) vs. Thickness (μm)

- RC rime constant @1 Hz
- RC time constant @10Hz

RC time constants: linear dependence with thickness
- Compromise between $G'$ and $\sigma$.
- SOS based gels exhibit higher modulus and conductivity than the SMS gels due to the smaller molecular weight and lower glass transition of the mid-block.
Optimizing Gel by Optimizing Block Polymer

PS  mid-block  PS

• Controls melting point
e.g. in [EMI][TFSA]
~4 kDa $M_n \rightarrow T_{gel} > 100 ^\circ C$.

• Must have Low $T_g$
• $M_n$ trade-off: $\sigma$ and $G$

$$G \sim \frac{ck_B T}{M_n} \quad \sigma = \sigma_s \left( \frac{1 - \phi_{PS}}{1 + \phi_{PS}} \right)^2$$

• Controls melting point
e.g. in [EMI][TFSA]
~4 kDa $M_n \rightarrow T_{gel} > 100 ^\circ C$.

e.g. Poly(ethyl acrylate) ($T_g \approx -24 ^\circ C$) in [EMI][TFSA],
20 wt% copolymer

$G \sim 10^4 \text{ Pa}, \quad \sigma > 10^{-3} \text{ S/m} @ 25 ^\circ C \rightarrow M_n \sim 20 \text{ kDa}$
### Conductivities of Electrolytes and Their Applications

<table>
<thead>
<tr>
<th>Conductivity Range</th>
<th>Electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-6}$</td>
<td>PEO/LiClO$_4$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>MEEP/LiTFSI</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>Ion Gel Electrolytes</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>Acidic Electrolytes</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td></td>
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</tbody>
</table>

#### Applications

- **Sensors (pressure)**
  - **Takao Someya**
  - Japan Radio Co., Ltd.

- **Supercapacitors & Batteries**
  - **Barbar Akle**

- **Actuators**
  - **Siemens**

- **Electrochromic displays**