Lessons from the beamline:  
The TES detector at beamline 10-1  
Charles J. Titus
How does hemoglobin transport oxygen?

How does iron bind to oxygen in hemoglobin? Pauling’s first model published in 1936. Can X-ray spectroscopy solve this 80-year old mystery?

Controversy: whose model is best?

Outline

- The TES advantage
- Science at SSRL using a TES
  - Understanding battery degradation
  - Detecting contaminants in carbon nanotubes
  - Measuring the Fe-O bond in hemoglobin
A hole in detector capabilities

Solid-state detectors

Resolving Power ($E/\Delta E$)

Solid Angle (sr)

$10^{-3}$

$10^{-4}$

$10^{-5}$

$10$ $100$ $1000$ $10000$
Can be filled by TES detectors!

Solid-state detectors

Transition-Edge Sensors

Diffraction Gratings

Resolving Power ($E/\Delta E$)

Solid Angle (sr)

1e-5
1e-4
1e-3

10
100
1000
10000

Photo credit D. Schmidt

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### TES at SSRL BL 10-1 available for users since 2017

#### Array Specs

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pixels</td>
<td>240</td>
</tr>
<tr>
<td>Solid Angle</td>
<td>2e-3 sr</td>
</tr>
<tr>
<td>Energy range</td>
<td>200-2000 eV</td>
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#### Pixel Specs

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<tr>
<td>Mo/Cu bilayer thickness</td>
<td>60 nm/200 nm</td>
</tr>
<tr>
<td>Tc</td>
<td>107 mK</td>
</tr>
<tr>
<td>Energy Resolution</td>
<td>1.5 eV @ 500 eV</td>
</tr>
<tr>
<td>Absorber thickness</td>
<td>2.8 um Bi</td>
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</table>

#### Samples

System details in
What causes thermal degradation of batteries?

Li et al, *J. Am. Chem. Soc.* 2019 (Accepted)
TES reveals that oxidation is the culprit

- Small changes in oxygen spectra indicate oxidation
- This work possible at SSRL for the first time, due to TES
What is contaminating carbon nanotube devices?

- TES shows a bunch of weird metals!
- Contaminants (<0.1%) affect device function
- TES more sensitive than other common probes (XPS)

XPS Composition Analysis vs TES Composition Analysis
How well can we measure ultra-dilute samples?

<table>
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<tr>
<th>Atomic %</th>
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![Graph showing XAS of diluted Fe(CN)$_6$]

How well can we measure ultra-dilute samples?

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XAS of diluted Fe(CN)$_6$

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XAS of diluted Fe(CN)$_6$

Excellent measurements of ultra-dilute samples

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<tr>
<td>0.001% (ultra-dilute)</td>
<td>Photosystem-II, doped monolayers, trace impurities, color centers</td>
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New capability: 0.001% measurement opens many doors!

So can we measure hemoglobin?
Yes!

TES has the sensitivity to reveal the Fe L-edge of hemoglobin for the first time.
First soft X-ray spectrum for oxyhemoglobin

Hemoglobin project in collaboration with:

**Stanford University**
- Leland Gee
- Augustus Braun
- James Yan
- Ed Solomon

**University of Manchester**
- Michael Baker

Who is right? Analysis is ongoing!

- **Pauling**
  - $\text{Fe}^{II} (S = 0) \cdot \text{O}_2 (S = 0)$

- **Weiss**
  - $\text{Fe}^{III} (S = 1/2) \cdot \text{O}_2^{-} (S = 1/2)$

- **McClure-Goddard**
  - $\text{Fe}^{II} (S = 1) \cdot \text{O}_2 (S = 1)$
Conclusions

- Robust beamline instrument with strong user demand
- TES enables battery measurements previously impossible at older light-sources
- A fast, non-destructive probe of composition
- TES enables new science in dilute compounds
Extra Slides
TES at SSRL BL 10-1

Beamline 10-1 parameters

<table>
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<th>Value</th>
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<tr>
<td>Photon Flux</td>
<td>$\sim 10^{11}$ phot/s</td>
</tr>
<tr>
<td>Energy Range</td>
<td>150-1400 eV</td>
</tr>
<tr>
<td>TES-sample distance</td>
<td>40 mm</td>
</tr>
<tr>
<td>Vacuum</td>
<td>$10^{-8}$ torr</td>
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Soft X-ray Spectroscopy (150 eV - 1500 eV)

Element-specific probe of:
- Chemical composition
- Electronic structure
- Spin
- Symmetry

L-edges (2p)
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn

K-edge (1s)
- B
- C
- N
- O
- F

Absorption

Emission

Resonant Scattering
X-ray Absorption Spectroscopy (XAS)

A photon is absorbed and kicks an electron to a higher energy level

Metal 2p states

Metal 3d states

XAS of Fe(CN)$_6^-$

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X-ray Absorption Spectroscopy (XAS)

A photon is absorbed and kicks an electron to a higher energy level

Metal 3d states
Metal 2p 3/2 states

Incident Energy (eV)

XAS Intensity

XAS of Fe(CN)$_6$

L3 edge

Incident Photon

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X-ray Emission Spectroscopy (XES)

A photon is emitted when an electron fills a core hole

Emitted Photon

Metal 3d states

Metal 2p 3/2 states

XES of Fe(CN)₆

Emitted Energy (eV)

XES Intensity

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Resonant Inelastic X-ray Spectroscopy (RIXS)

Absorption and emission are linked together in a resonant process

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Routine Spectroscopy

Requirements

- Moderate solid angle
- Moderate energy resolution

Applications

- Everything

Carsch et al, 2019 (In revision)