Characterizing energy storage nanomaterials by synchrotron light

J. G. Zhou, J. Wang, and J. N. Cutler
Canadian Light Source Inc., Canada
T.K. Sham
University of Western Ontario
H.T. Fang
Harbin Institute of Technology, China

PHEV'09 Montreal September 2009

Motivations

Better energy storage devices for HPEV
(Long life, safety, high performance/cost)

↓

nanomaterials

Structure ⟶ Property ⟶ Performance

Canadian Light Source Centre canadien de rayonnement synchrotron

Outline

1. X-ray Absorption Near Edge Structure (XANES) spectroscopy----TiO_2

2. Scanning Transmission X-ray Microscopy (STXM)----RuO_2/MWNT

Synchrotron light

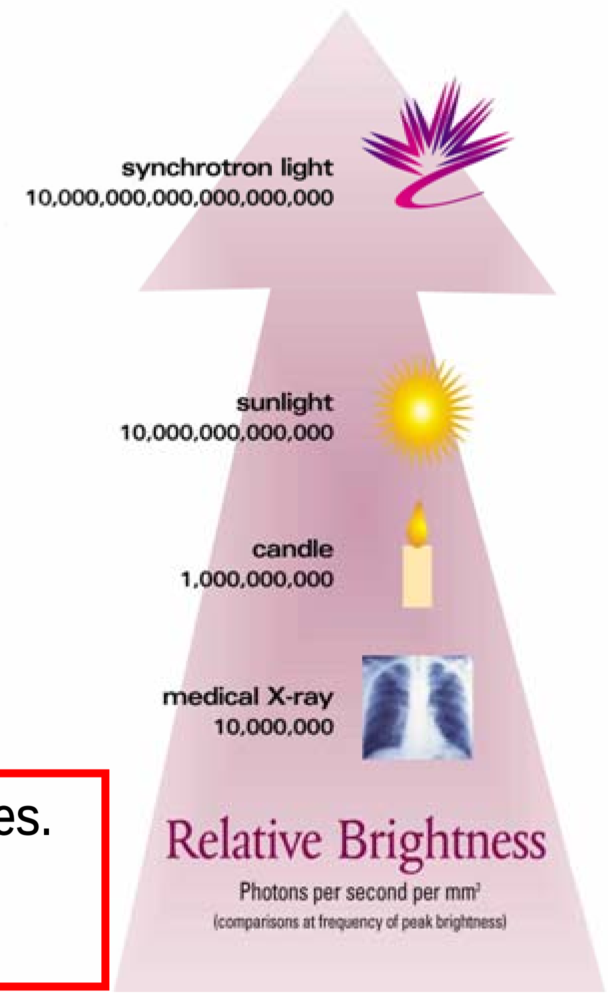
Synchrotron Radiation is Extremely Intense Light!!!

Infra-Red – Heat
Ultraviolet – Summer Tan
X-rays – Medical Exam

How is Synchrotron Light Produced?

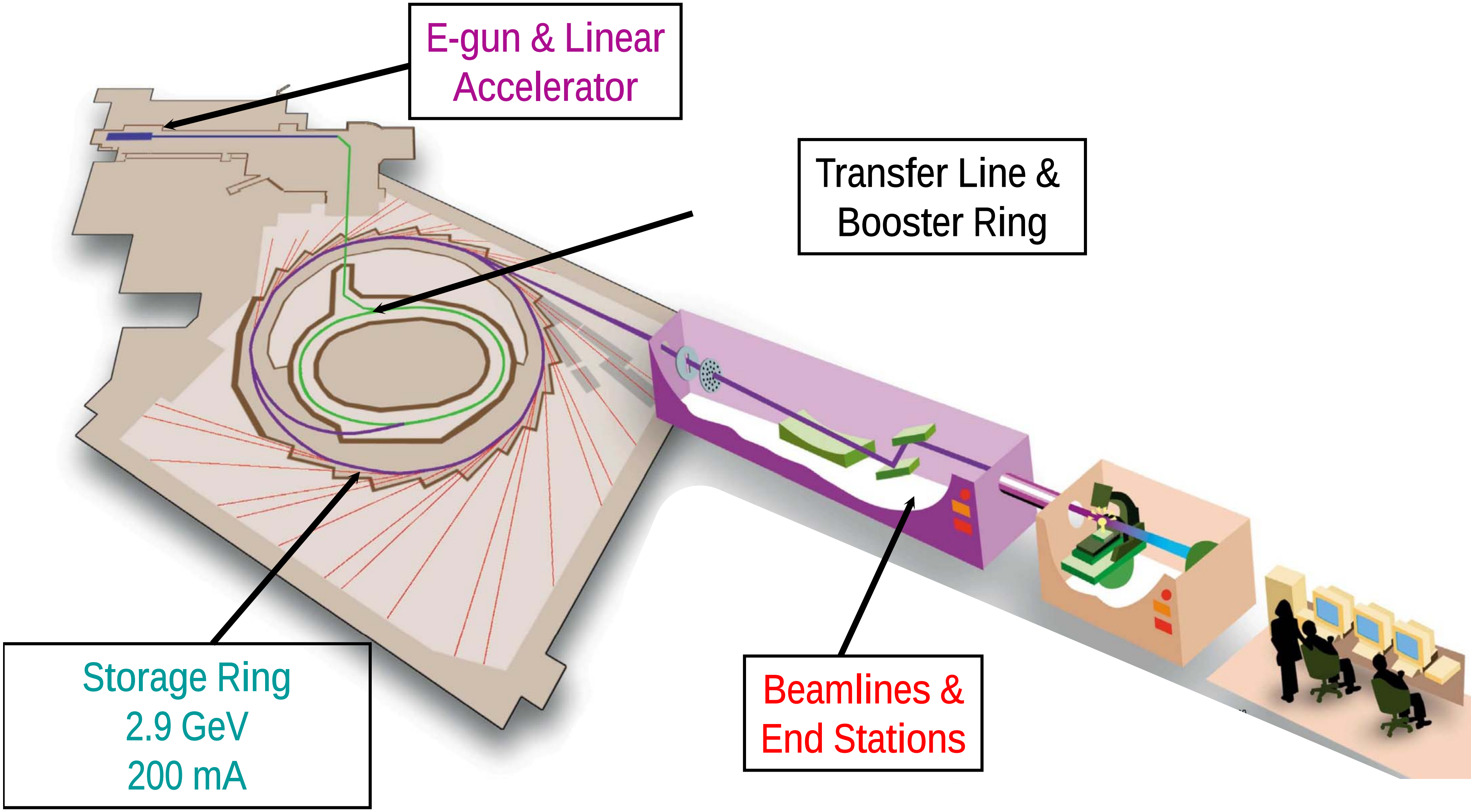
Light is produced by the Acceleration of Charged Particles.

In Synchrotron Facilities, these Particles are Electrons



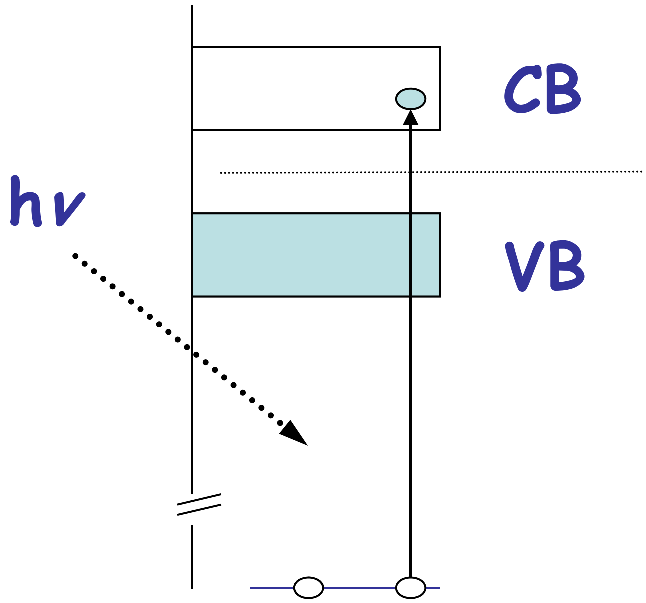
Canadian Light Source Centre canadien de rayonnement synchrotron

Light Source

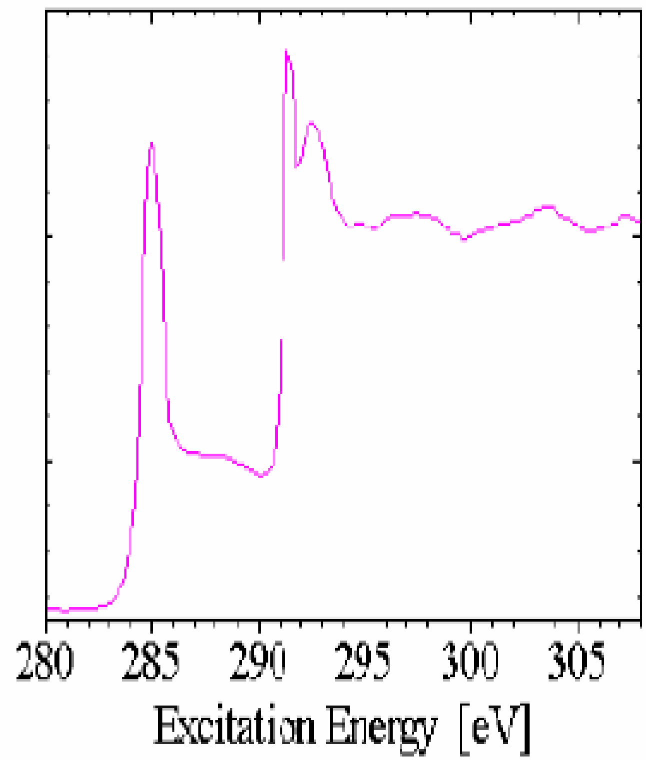


Canadian Light Source (CLS)

X-ray Absorption Near Edge Structure (XANES) spectroscopy



Excitation



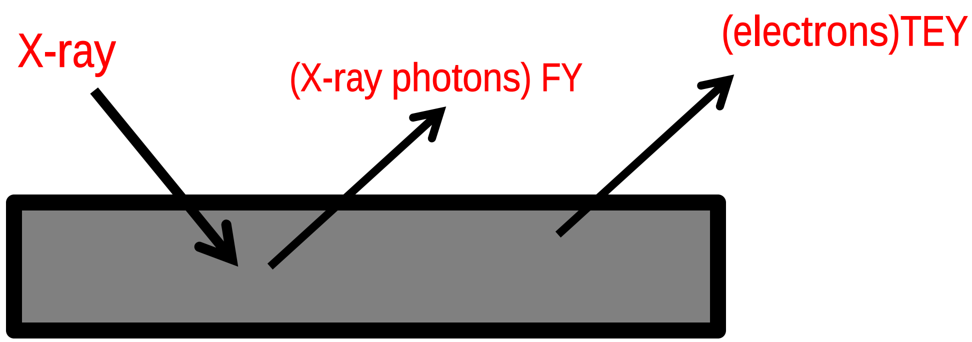
XANES spectroscopy is useful in :

Chemical Analysis: Finger print approach

Geometric Structure: Molecular Orientation

Electronic Structure: Unoccupied Density of States

XANES detection modes /probing depths

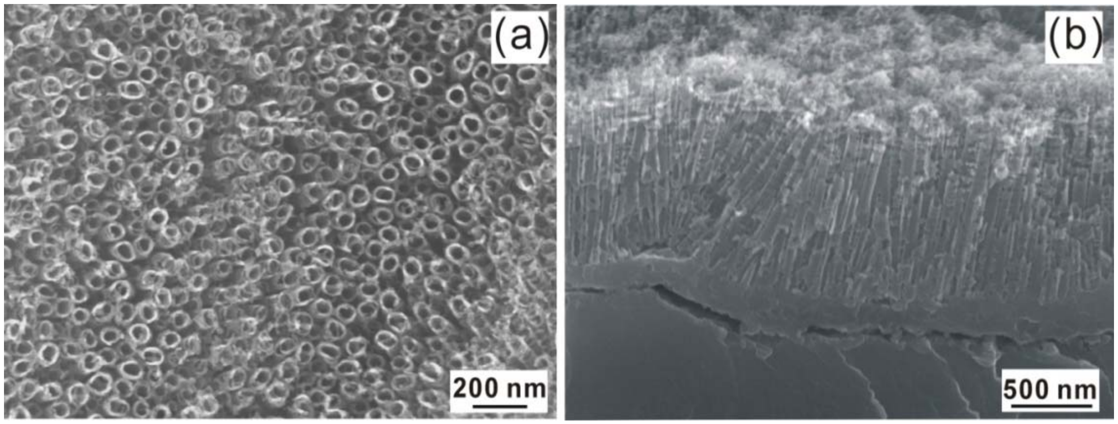


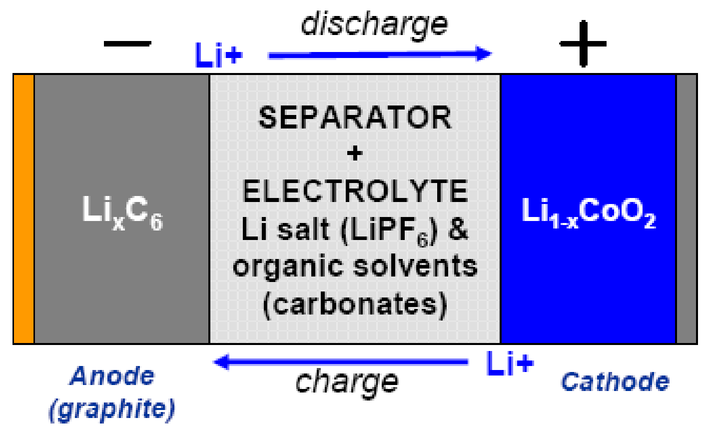
TEY: surface sensitive (10 nm probing depth)

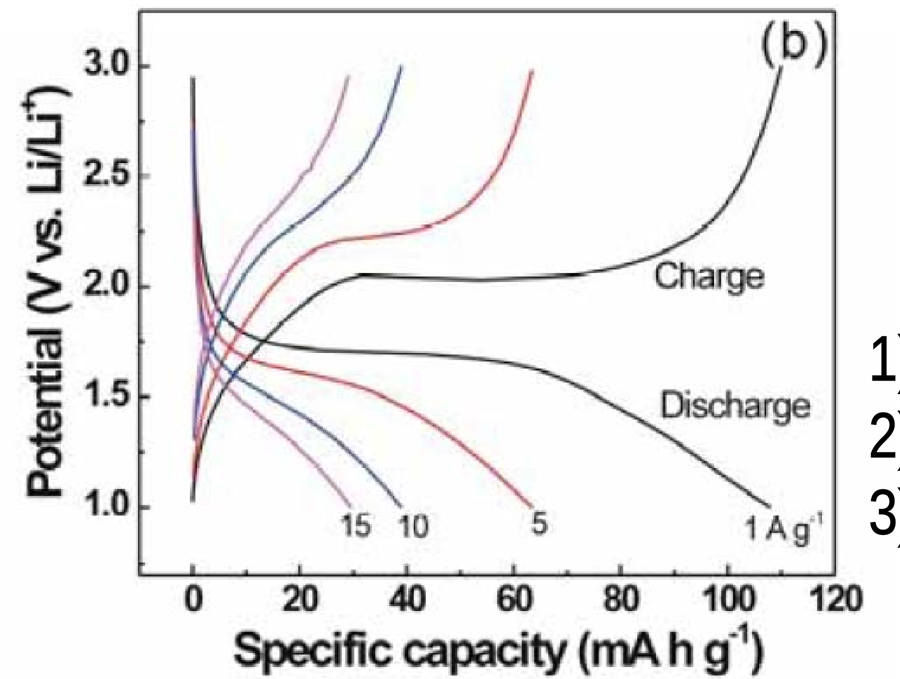
FY: bulk sensitive (100 nm probing depth)

Non-destructively differentiate layered structures

TiO_2 nanotube arrays study by XANES



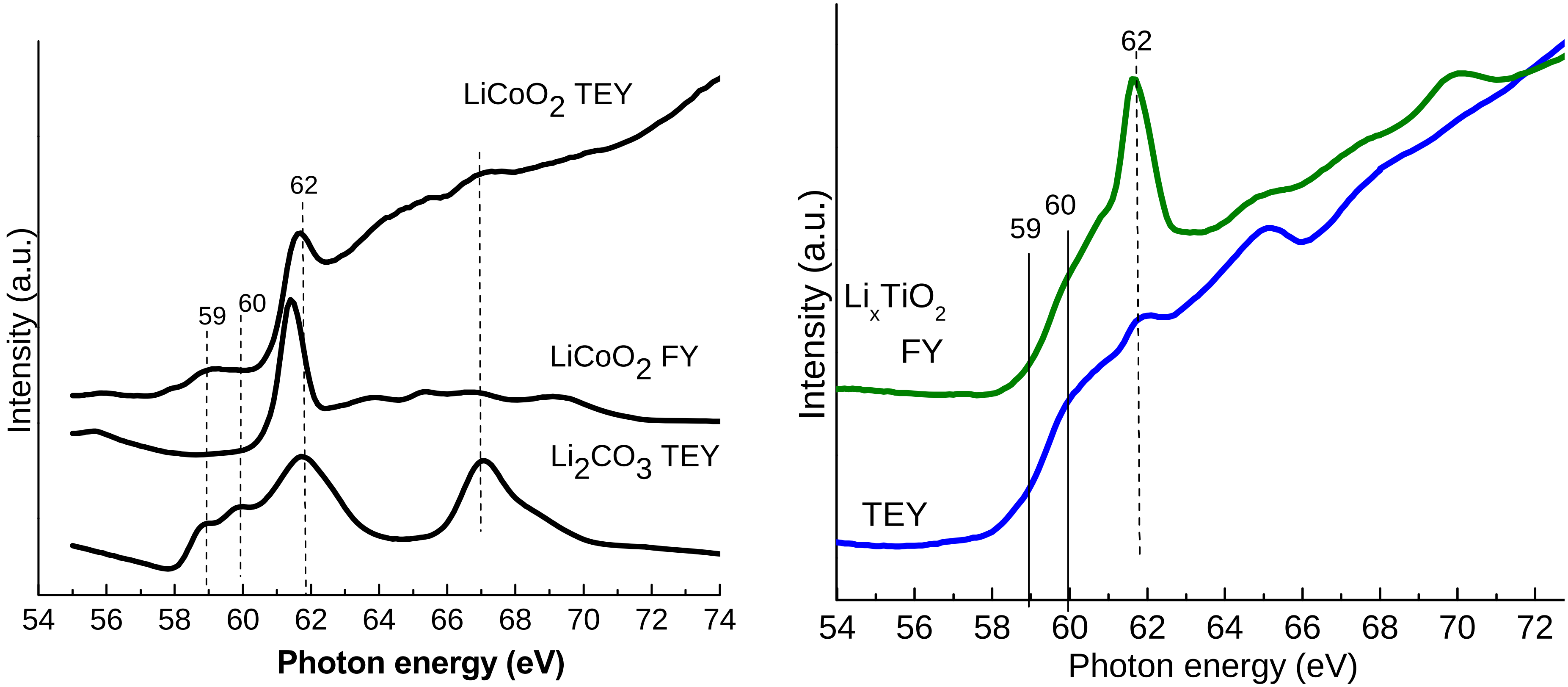




Why do we need TiO_2

1)Safe - higher Li intercalation potential
2)Capacity - more Li storage
3)High-rate - fast charge/discharge

Chemical identification of Li in Li_xTiO_2

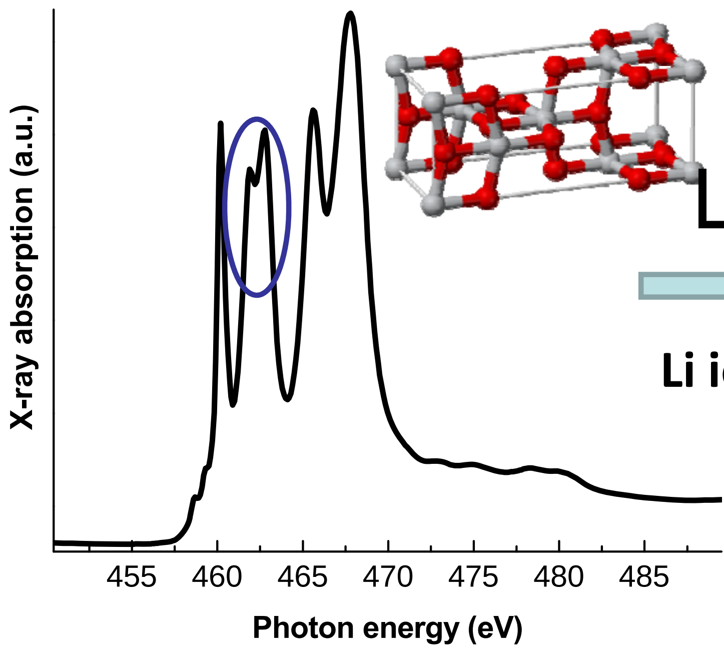


Li K-edge XANES in Li_xTiO_2 :

1) Li^+ but not Li metal is in Li_xTiO_2 ; 2) Surface of Li_xTiO_2 is covered by Li_2CO_3

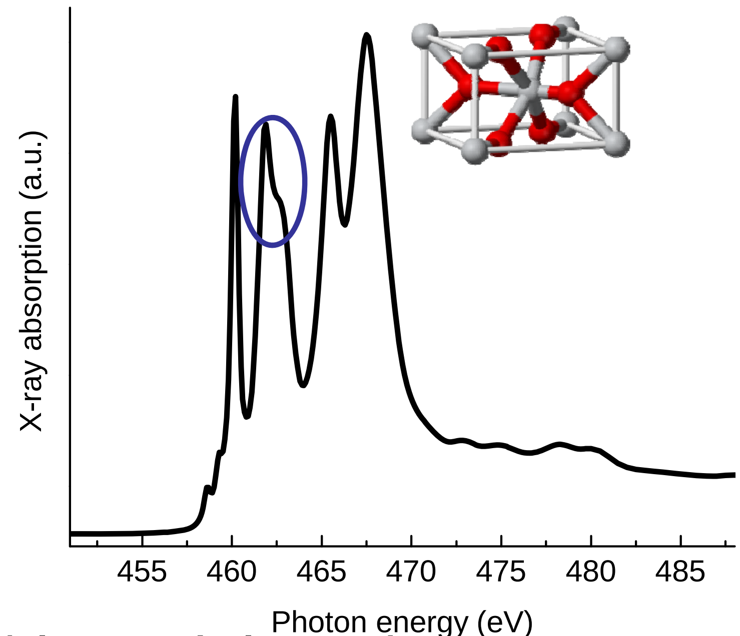
J.G. Zhou, et al, J MC 2009

Charge compensation along Li intercalation



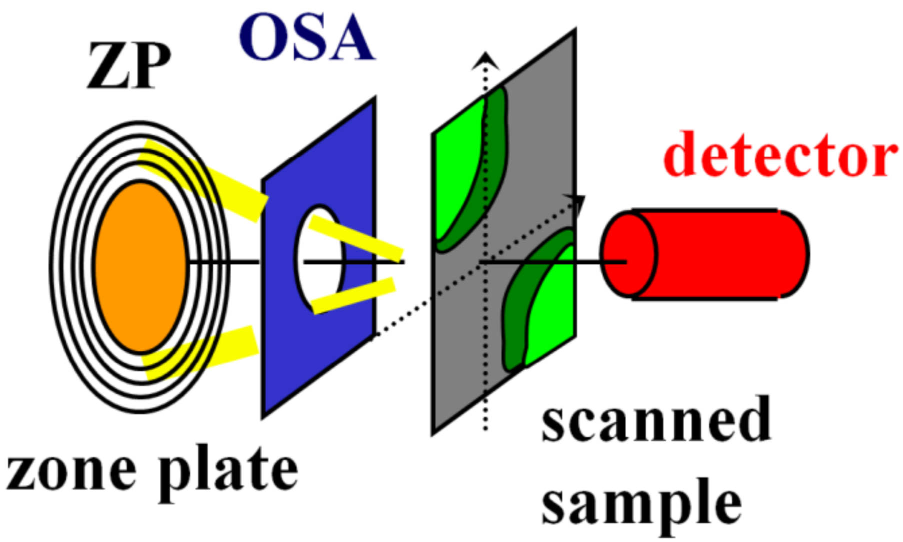
$Li^{+}+e^{-}+TiO_2$

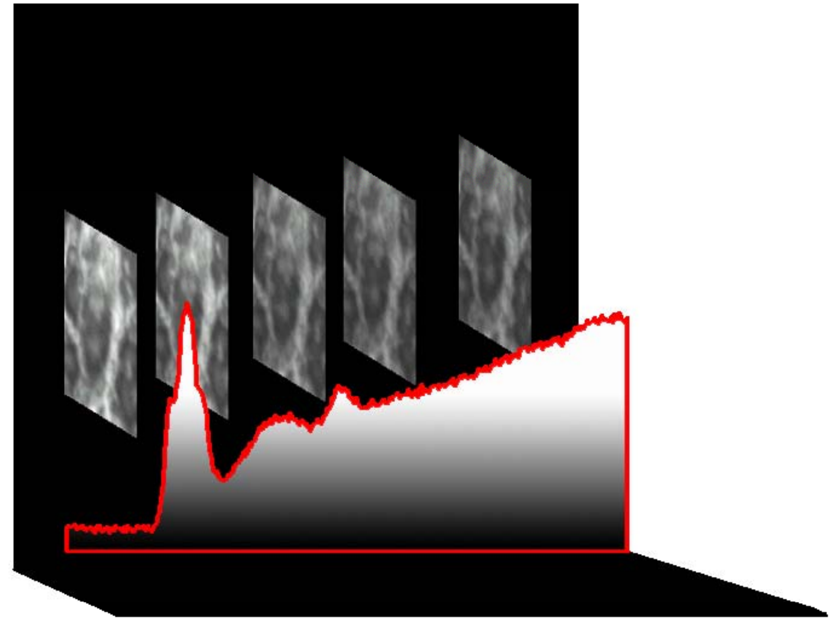
Li ion intercalation



1) Li intercalation doesn't produce detectable Ti^{3+} (electron is located at O sides, evidenced by the reduction in O K-edge XANES)
2) Li intercalation results in the phase transition in a fully intercalated TiO_2. (It will be valuable to monitor the process by an in-situ XANES and study if the phase transition is reversible.) *J.G. Zhou, et al, J MC 2009*

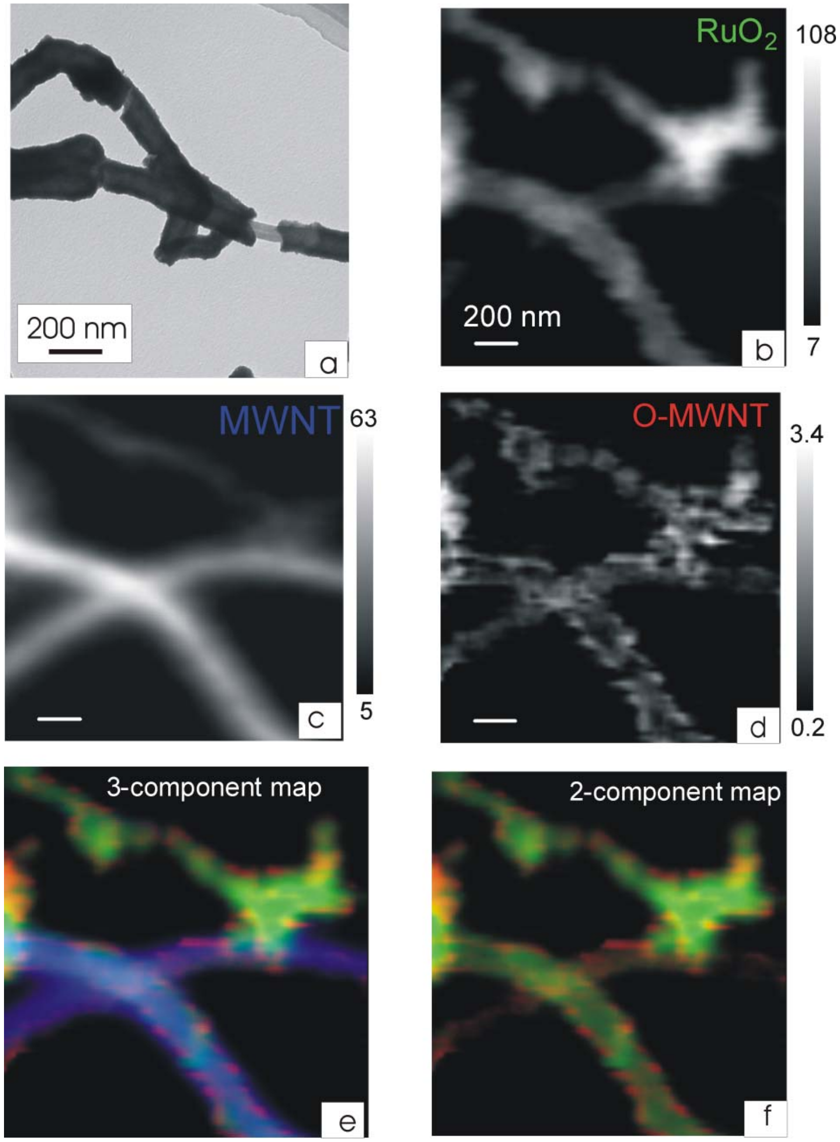
Scanning Transmission X-ray Microscopy (STXM)





- A transmission image is captured *at each* step (typically 0.05 eV) scanned across a specific region.
- Compiled to created a 3-D data array. It is called STXM image stacks.
- Fitting procedures are used to create chemical species maps;Extraction of spectra from single pixels or groups of pixels can be done with a 30 nm spatial resolution.

Nanoscale chemical imaging of isolated RuO_2/MWNTs

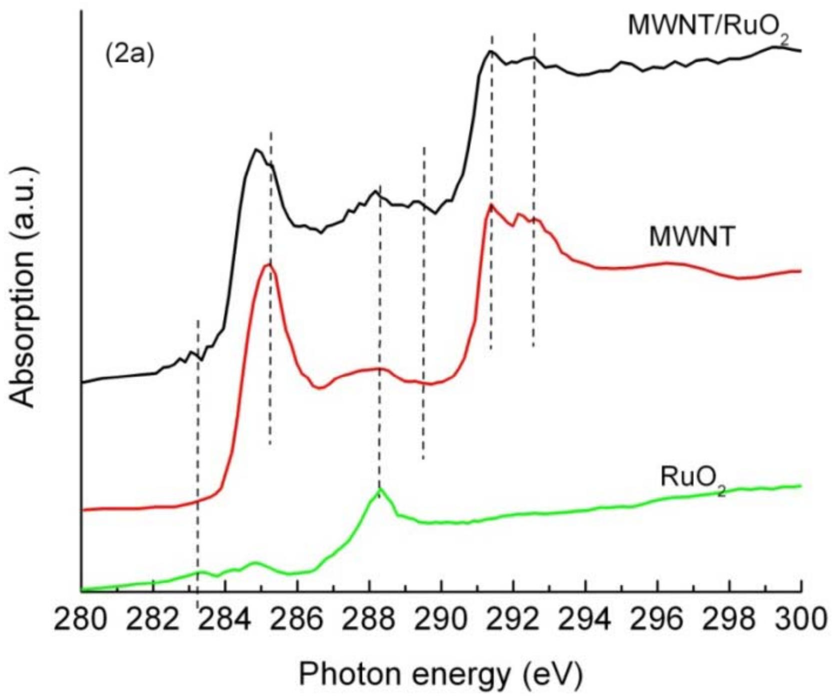


TEM: RuO_2 coating (thickness of ~ 20 nm) on MWNTs (diameter of ~ 65 nm). Chemistry is missing.

Quantitative chemical imaging at 30 nm scale RuO_2 coating is not homogeneous ;oxygen functional group density is slightly increased relative to the density prior to RuO_2 coating

The color composite map of RuO_2, MWNT and oxygen-containing functional groups in the individual RuO_2/MWNT can be generated.

spectroscopy of isolated RuO_2/MWNTs



Coating RuO_2 results in charge transfer from RuO_2 to CNT :

a) A new peak (289.3 eV), corresponding to the Ru-O-C bonding

b) Less DOS in Π^*

c) Peak of 285 eV shifts to lower energy.

Summary

1. XANES has been successfully applied to investigate the chemical bonding, electronic structure, and surface chemistry of Li intercalated TiO_2.

2. Scanning transmission X-ray microscopy (STXM), based on the X-ray absorption process, has a chemical contrast mechanism for imaging RuO_2 coated CNTs at the nano-scale.

Canadian Light Source
Centre canadien de rayonnement synchrotron

Funding Partners

Canada Foundation for Innovation
Fondation canadienne pour l'innovation

NSERC CRSNG

Canada
National Research Council Canada
Conseil national de recherches Canada

CIHR IRSC
Canadian Institutes of Health Research
Instituts de recherche en santé du Canada

Government of Saskatchewan

Canada
Western Economic Diversification Canada
Diversification de l'économie de l'Ouest Canada

Alberta
INNOVATION AND SCIENCE

UNIVERSITY OF SASKATCHEWAN

ALBERTA HERITAGE FOUNDATION FOR MEDICAL RESEARCH

BRITISH COLUMBIA

Ontario

Ontario Innovation Trust

Ressources naturelles Canada
Natural Resources Canada

SaskPower

UNIVERSITY OF ALBERTA
QUAECUMQUE VERA

City of Saskatoon

Boehringer Ingelheim

Western

Rockwell Collins

38 supporting University Partners and growing…

Acknowledgements

Technique support

Dr. L. Zuin at PGM

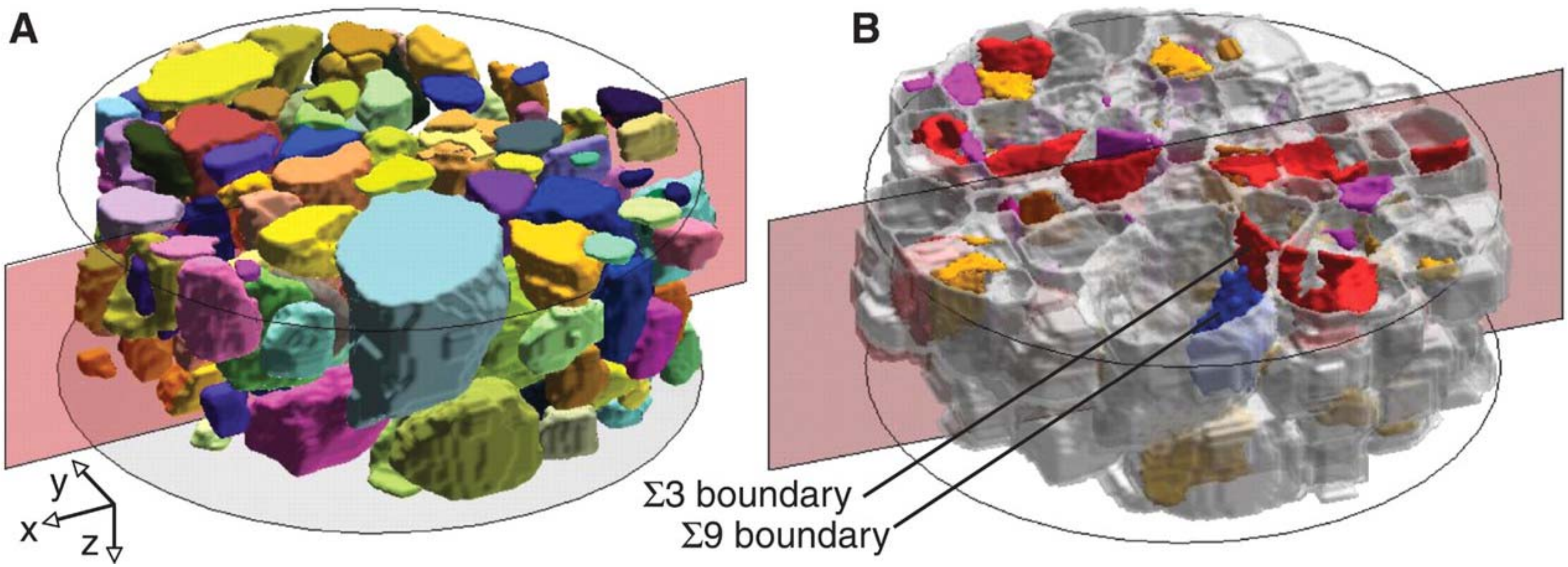
Dr. R. Blyth and Mr. T. Regier at SGM

Dr. Chithra Karunakaran, and Mr. Y.S. Lu at SM


Thanks!

Materials characterization by hard X-rays

3) Computed tomography: absorption or diffraction contrast

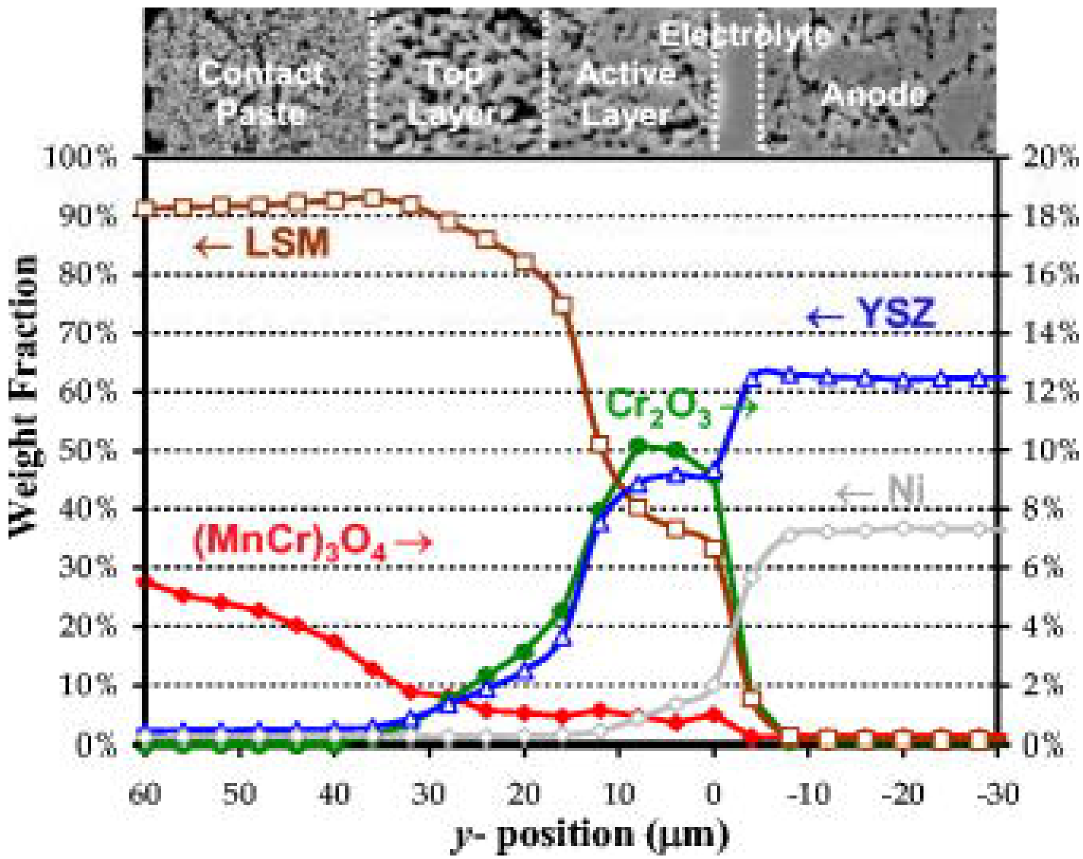


The Diffraction contrast CT data provides a 3D map of the grain shapes and their crystal orientations, which is useful for stress corrosion study. (Science 321, 382 (2008))

It should be a valuable tool in studying the porous electrodes

Materials characterization by hard X-rays

1) Microprobe + X-ray diffraction = 2D/3D composition/strain mapping



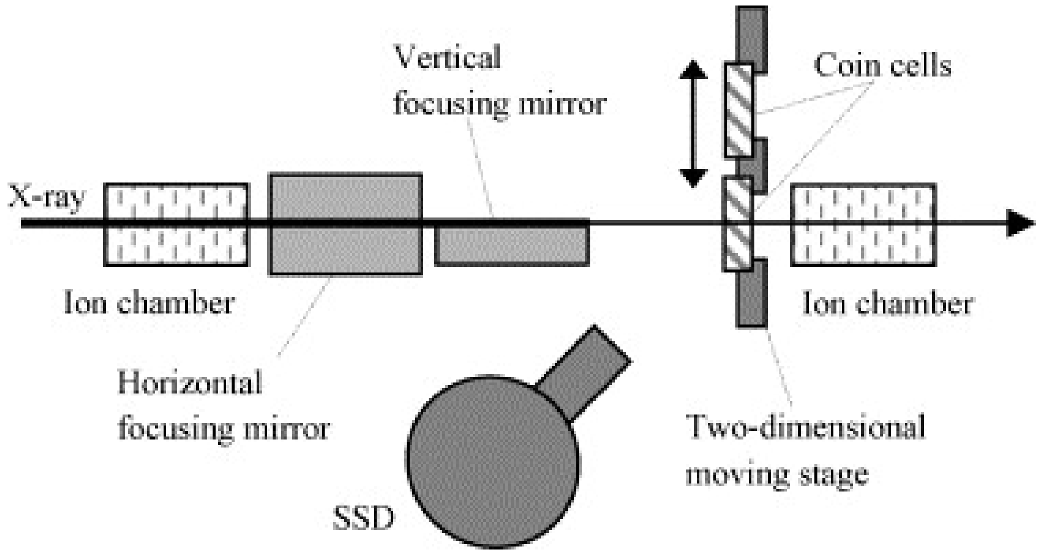
2D distributions of phase fractions, internal strains, and their interdependences inside of a planar SOFC deactivated by Cr contamination has been obtained .

Due to strong penetration of hard x-rays and high spatial resolution, this can further investigate SOFC and other layered electrochemical devices under actual operating conditions.

APL 94, 224106 (2009)

Materials characterization by hard X-rays

2) In situ XAFS (XANES and/or EXAFS) on electrodes for Li-ion battery

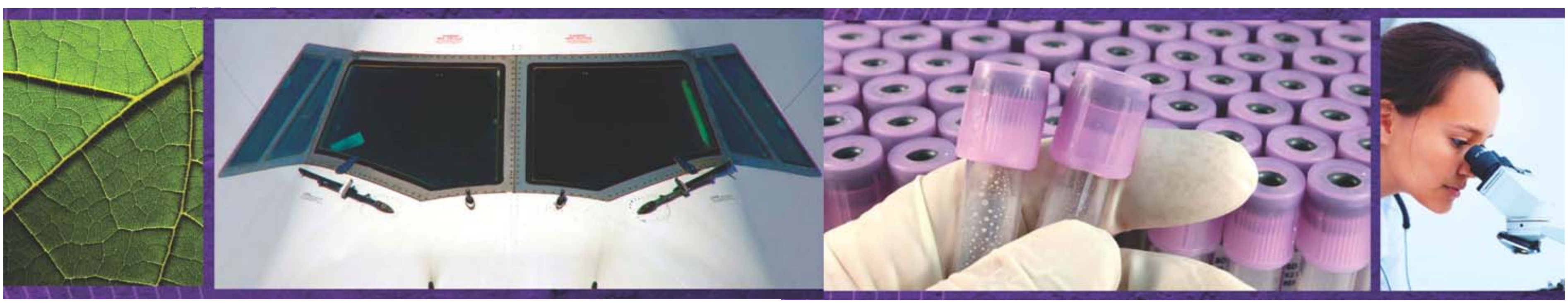


In situ XAFS is a powerful tool to provide an understanding of oxidation state as well as short-range order structure, which may not be accessible from X-ray diffraction, without destroying batteries for measurements

J. Power Source 162 (2006) 1329

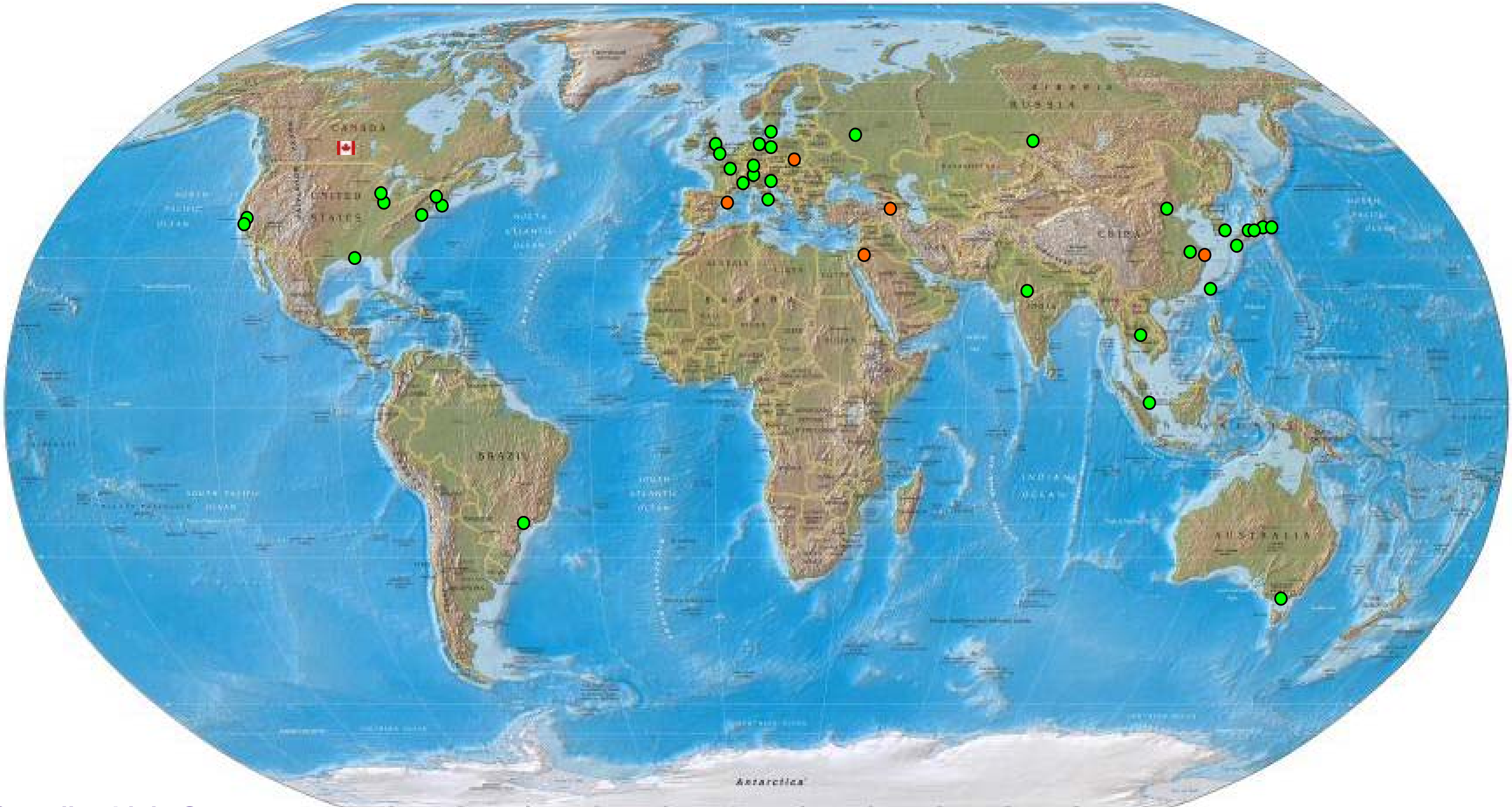
Canadian Light Source Inc.
Centre canadien de rayonnement synchrotron

Canadian Light Source Inc.
(Canadian National Synchrotron Research



Synchrotrons of the world

There are approximately 40 similar synchrotron facilities in 20 countries around the world



Canadian Light Source

Synchrotrons currently in operation

Synchrotrons under construction or in planning phase

Phase I Beamlines - Operational

Beamline (Port)	Energy (eV) (cm^{-1} for IR) / Wavelength (Å) (µm for IR)		Resolution	Flux (γ/s/0.1%BW) @ 500 mA / Spot size Hor x Vert	Techniques
Far Infrared Spectroscopy (Far-IR) (02B1-1)	10	1000	≥ 0.001 cm^{-1} ΔE	1×10^{13} @ 100 µm	Fourier Transform Absorption Spectroscopy: - <u>Gas phase</u> - Stable - 2 m cold multi-reflection (M-R) cell - 0.3 m ambient M-R cell - Radicals - 1.5 m hollow cathode M-R cell - 1.2 m furnace/discharge M-R cell - <u>Condensed phase</u> - High-pressure - Diamond Anvil Cell - Surface - Grazing Angle Incidence - Attenuated Total Reflectance - Photo-Acoustic
	1000	10		Diffraction limited λ / 2	
Mid Infrared Spectromicroscopy (Mid- IR) (01B1-1)	750	6000	16.0 – 0.125 cm^{-1} ΔE	1×10^{14} @ 10 µm	Spectromicroscopic imaging at diffraction-limited spatial resolution Spectromicroscopy at grazing angle of incidence Spectromicroscopy with Attenuated Total Internal Reflection (ATR) Photoacoustic Emission Spectroscopy
	13.3	1.7		Diffraction Limited λ / 2	
Variable Line Spacing Plane Grating Monochromator (VLS PGM) (11ID-2)	5.5	250	>10,000 E/ΔE	2×10^{12} @ 80 eV	X-ray Absorption Spectroscopy (XAS) X-ray Excited Optical Luminescence (XEOL) Photoemission Electron Microscopy (PEEM)
	2250	50		500 µm x 500 µm	
High Resolution Spherical Grating Monochromator (SGM) (11ID-1)	240	2000	> 5000 E/ΔE	2×10^{13} @ 500 eV 6×10^{11} @ 1900 eV	X-ray Absorption Spectroscopy (XAS) X-ray Photoelectron Spectroscopy (XPS) Auger Electron Spectroscopy (AES) X-ray Excited Optical Luminescence (XEOL) Gas phase photoionization and TOF measurements
	50	6.2		50 µm x 100 µm	
Soft X-ray Spectromicroscopy (SM) (10ID-1)	100	2000	3000 – 7000 E/ΔE	~ 10^{8} in 50 nm spot	Scanning transmission X-ray Microscopy (STXM) Photoemission Electron microscopy (PEEM) Circular Polarization: 100 – 1000 eV Linear Polarization: 100 – 2500 eV
	125	6.2		~ 10^{12} in 50 µm spot	
Canadian Macromolecular Crystallography Facility (CMCF) (08ID-1)	6500	18000	10^{-4} ΔE/E	10^{13}	Single crystal X-ray diffraction Multiwavelength Anomalous Dispersion (MAD)
	1.9	0.7		150 µm x 50 µm	
Hard X-ray MicroAnalysis (HXMA) (06ID-1)	5000	40000	10^{-4} ΔE/E	~ 6×10^{11} Si(111) b.w ~ 7×10^{10} Si(111) b.w	X-ray Absorption Fine Structure (XAFS) Microprobe Diffraction
	2.5	0.3		XAFS:100 x 500 µm Microprobe: 2 x 4 µm	

Phase III

The Brockhouse X-ray Diffraction and Scattering Sector (Undulator)[2] (04ID-1)	3000	15000	Inelastic Scattering: 10^{-6}	10^{10} Into 100 µm X 100 µm	Inelastic Scattering Resonant Scattering Grazing Incidence Diffraction Reflectivity Small Angle X-ray Scattering Wide Angle X-ray Scattering
			Resonant Scattering: 10^{-4}	10^{12} Into 100 µm X 100 µm	
	4.1	0.8	Grazing Incidence Diffraction: 10^{-4}	10^{12} Into 100 µm X 200 µm	
			SAXS/WAXS:10^{-4}	10^{11} Into 200 µm X 100 µm	
The Brockhouse X-ray Diffraction and Scattering Sector (Wiggler)[2] (04ID-2)	7000	60000	Powder diffraction:10^{-4}	10^{11} Into 1000 µm X 200 µm	Powder Diffraction Single Crystal Crystallography High Pressure Diamond Anvil Cell High Q-space PDF
			Single crystal crystallography:10^{-3}	10^{10} Into 100 µm X 100 µm	
	1.8	0.2	High pressure diamond anvil:10^{-4}	10^{11} Into 25 µm X 25 µm	
			High Q space PDF:10^{-3}	10^{11} Into 500 µm X 500 µm	
BioXAS: Life Science Beamline for X-ray Absorption Spectroscopy (Wiggler)[2] (07ID-1)	5000	28000	10^{-4}	9×10^{12} into 600 µm X 200 µm	Bulk X-ray Absorption Fine Structure at low and ultra-low concentrations and high resolution with automation for "FedEXAFS" XAS Imaging: Macro (>50 mm), Micro (~2 mm), and Sub-Micro (<1 to ~2mm)
	2.5	0.4			
BioXAS: Life Science Beamline for X-ray Absorption Spectroscopy (Undulator)[2] (07ID-2)	5000	15000	10^{-4}	2×10^{13} into 400 µm X 20 µm	XAS Imaging: Macro (>50 mm), Micro (~2 mm), and Sub-Micro (<1 to ~2mm)
	2.5	0.8			
The Quantum Materials Spectroscopy Centre (EPU1 225 mm period)[2] (09ID-1)	10	200	NA	Brilliance: 7×10^{16} Spin: 400 µm X 40 µm 400 µm X 40 µm (at 30 eV)	Spin and angle resolved photoemission spectroscopy Separate organic and inorganic Molecular Beam Epitaxy and characterization chambers
	1240	62			
The Quantum Materials Spectroscopy Centre (EPU2 54 mm period)[2] (09ID-2)	200	1000	NA	Brilliance: 7×10^{17} Spin: 700 µm X 40 µm ARPES: 300 µm X 40 µm (at 200 eV)	Spin and angle resolved photoemission spectroscopy Separate organic and inorganic Molecular Beam Epitaxy and characterization chambers
	62	12			

Phase II - Under Construction

Beamline (Port)	Energy (eV)		Wavelength (Å)		Resolution (ΔE/E)	Flux (γ/s/0.1%BW) @ 500 mA	Spot size Hor x Vert	Techniques
Resonant Elastic and Inelastic X-ray Scattering (REIXS)[1] (10ID-2)	80	2000	155	6.2	1×10^{-4} @100 eV 2×10^{-4} @1000 eV	2×10^{13} @ 100 eV 5×10^{12} @ 1000eV	250 μm x 15 μm 60 μm x 10 μm	X-ray Absorption Spectroscopy X-ray Emission Spectroscopy Resonant Inelastic X-ray Scattering Resonant Elastic X-ray Scattering Coherent X-ray Scattering (Speckle) Magnetic X-ray Dichroism Molecular Beam Epitaxy sample preparation
Soft X-ray Microcharacterization Beamline (SXRMB)[1] (06B1-1)	1700	10000	7.3	1.3	3.3×10^{-4} InSb (III) 1×10^{-4} InSb (III)	XAFS: > 1×10^{11} Microprobe: 1×10^{9}	300 μm x 300 μm ~ 10 μm x 10 μm	X-ray Absorption Spectroscopy Microprobe X-ray Excited Optical Luminescence (XEOL) Resonant spectroscopies X-ray Magnetic Linear Dichroism (XMLD) Photo Emission Electron Microscopy (PEEM) X-ray Magnetic Circular Dichroism (XMCD) Photo and Auger Electron Spectroscopy
Synchrotron Laboratory for Micro And Nano Devices (SyLMAND)[1] (03B1-1 & 03B2-1)	1000	15000	12.4	0.82	NA	NA	150 mm x 15 mm	Deep X-ray lithography LIGA process lithography steps
Very Sensitive Elemental and Structural Probe Employing Radiation from a Synchrotron (VESPERS)[1] (07B2-1)	6000	30000	2	0.4	Si(111) – 10^{-4} MLM1 – 10^{-2} MLM2 – 10^{-1} Pink Beam	Si-111 ~ 2×10^{9} @ 15 keV MLM1 ~ 1×10^{11} @ 15 keV MLM2 ~ 4×10^{11} @ 15 keV	(2 – 4) μmx(2\– 4) μm	X-ray Laue Diffraction X-ray Fluorescence Spectroscopy X-ray Absorption Near Edge Structure Differential Aperture X-ray Microscopy Multi-bandpass and pink beam capability
Canadian Macromolecular Crystallography Facility (CMCF 2)[1] (08B1-1)	4000	18000	3.1	0.69	10^{-4}	10^{12} @ 12 keV	230 μm x 160 μm	X-ray diffraction Multiwavelength Anomalous Dispersion (MAD)
Biomedical Imaging and Therapy (BMIT - BM)[1] (05B1-1)	8000	40000	1.6	0.3	M1 DEI: 10^{-4}	1.5×10^{13} @ 10 keV	231 mm x 4.6 mm @ 23 m	Conventional absorption imaging Diffraction Enhanced Imaging (DEI) / Multiple Image Radiography (MIR) Phase contrast or in-line holography Ultra-small, small, wide angle scattering imaging Computer Tomography (CT)
Biomedical Imaging and Therapy (BMIT - ID)[1] (05ID-1 & 05ID-2)	20000	100000	0.6	0.1	M1 CT:10^{-3} M2 CT:10^{-3} M3 DEI:10^{-5} M4 KES:10^{-3}	4×10^{14} @ 40 keV	224 mm x 11.2 mm @ 56 m	Imaging – conventional absorption imaging, DEI / MIR, CT, K-edge Subtraction (KES) Therapy – Microbeam Radiation Therapy, CT Therapy

Canadian Light Source | Centre canadien de rayonnement synchrotron

Meeting the Needs of Business

- The Canadian Light Source (CLS) is Canada's national synchrotron research facility, where intense beams of light are generated to probe the nature and structure of matter.
- The CLS mandate includes active industrial participation with innovative commercial research access, clear intellectual property policies and scientists dedicated to promoting industry involvement.
- From mining, biotechnology and pharmaceuticals, the environment and health, to agriculture, nanotechnology, manufacturing and oil and gas, synchrotron science is a unique and invaluable tool for industrial research and development.