Scanning probe techniques & Spectroelectrochemistry (ch. 16/17)

Ch. 16
Scanning tunneling microscopy (STM)
Atomic force microscopy (AFM)
Scanning electrochemical microscopy (SECM)

Ch. 17
UV & visible spectroscopy
Vibrational spectroscopy: IR spectroscopy, Raman spectroscopy
Electron & ion spectroscopy: XPS, AES, mass spectroscopy
Quartz crystal microbalance
X-ray methods: XAS, XRD

Microscopy: optical → scanning electron → STM, AFM
in situ vs. ex situ techniques

Scanning tunneling microsocpy (STM)

Cell for *in situ* (electrochemical) STM

STM images of HOPG

In situ STM images of Pt(111) with I-adlattice in $HClO_4$

In situ STM images of Cu(111): effect of etching

Atomic force microscopy (AFM)

Cantilever displacement vs. z-deflection for (left) attractive interaction and (right) repulsive interaction

In situ AFM: Cu underpotential deposition (UPD) on Au(111)

Scanning electrochemical microscopy (SECM)

Principles of SECM

SECM approach curves for steady-state currents

Imaging surface topography & reactivity

Ta oxide formation on Ta

Commercialized SECM

SECM applications

Ag line formation

Electrochemical Cu etching

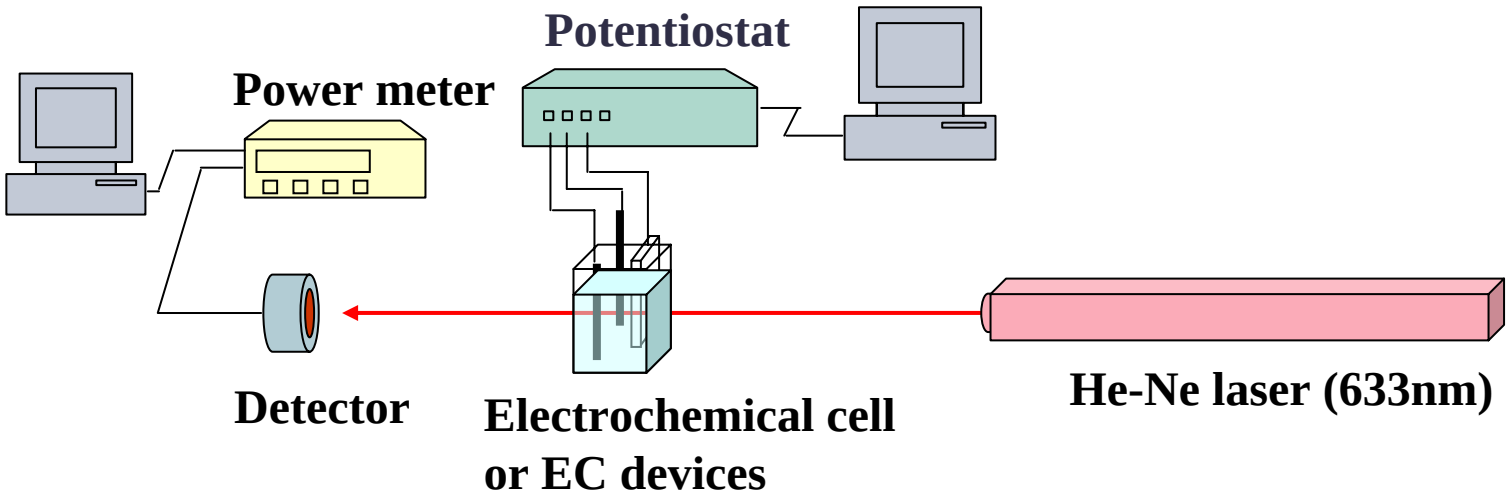
Spectroelectrochemistry (Ch. 17)

UV & visible spectroscopy

Transmission experiments

Spectra of cobalt complex at different potentials

In-situ transmittance test

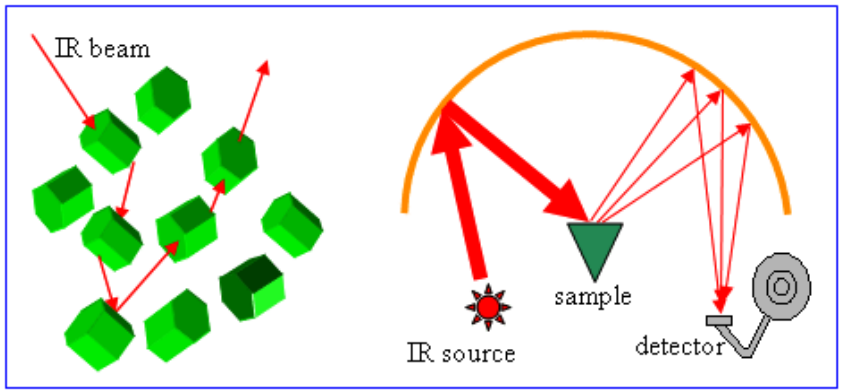


Vibration spectroscopy
Infrared spectroscopy

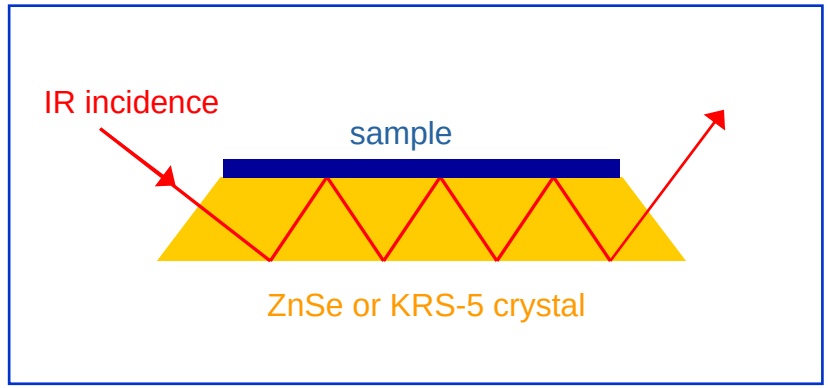
Infrared spectroelectrochemistry (IR-SEC)

In situ FT-IR spectroscopy

❖ **Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT)**



❖ **Attenuated Total Reflectance Spectroscopy (ATR)**

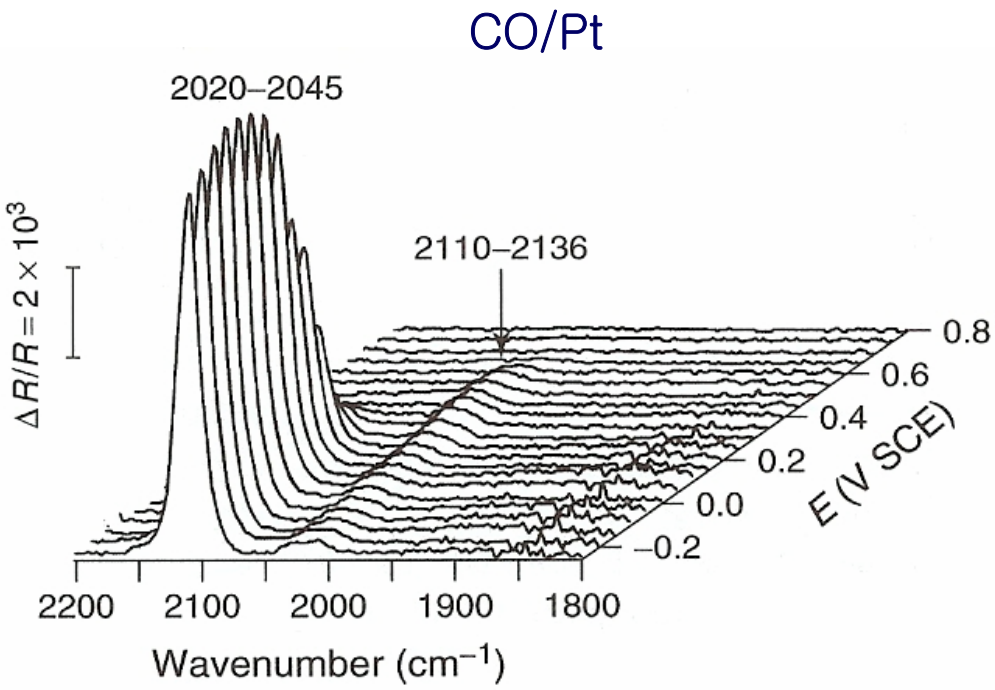


***Transmission measurement**
***Reflection-Aborption infrared Spectroscopy (RAS)**
***Photoacoustic Spectroscopy (PAS)**
***Surface Electromagnetic Wave spectroscopy (SEW)**

In situ FT-IR

***In situ* FT- IR cell**

In situ FT-IR

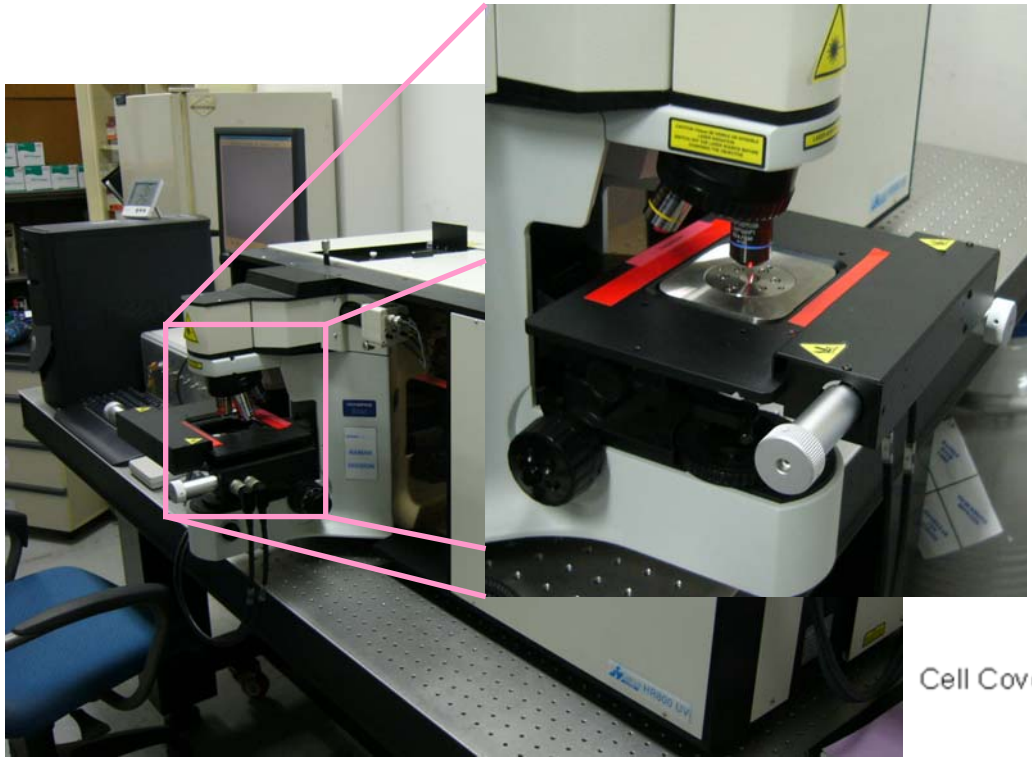

CO/Pt
2020–2045
2110–2136
$\Delta R/R = 2 \times 10^3$
0.8
0.6
0.4
0.2
0.0
–0.2
E (V SCE)
2200
2100
2000
1900
1800
Wavenumber (cm^{-1})

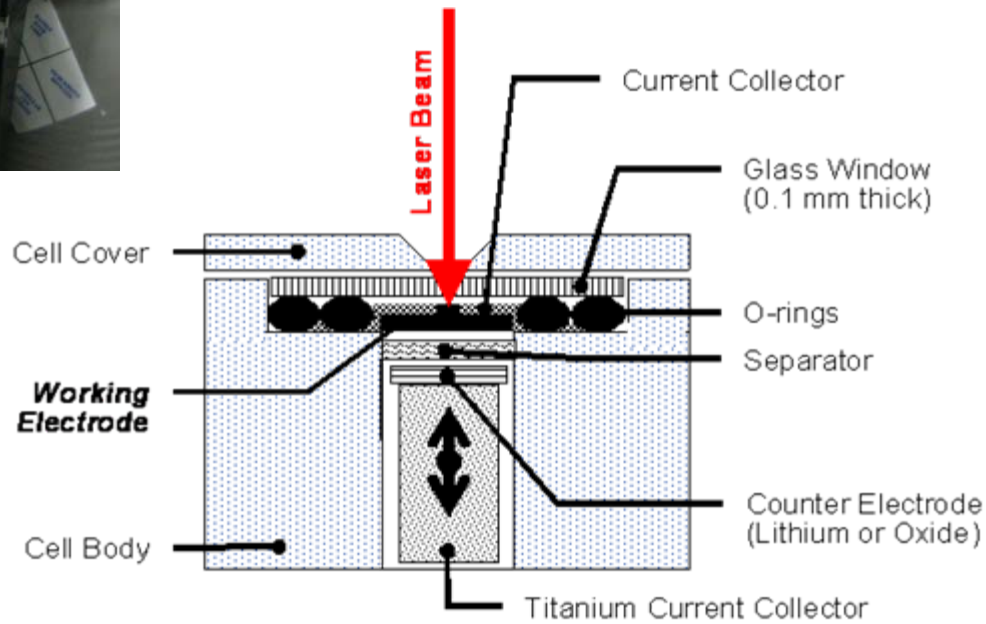
Raman spectroscopy

Raman spectroscopy: molecular vibrational information complementing IR spec.
Raman in electrochemical system: signal enhancement

- Resonance Raman spectroscopy (RRS)
- Surface enhanced Raman spec. (SERS): molecules adsorbed on certain surfaces (Ag or Au)

In situ Raman Spectroscopy





Electron and ion spectrometry

Ultra high vacuum (UHV)

	Excitation	Detection
X-ray photoelectron spectroscopy (XPS)	Photons(X-ray)	Electrons
UV photoelectron spectroscopy (UPS)	Photons (UV)	Electrons
Auger electron spectroscopy (AES)	Electrons	Electrons
Low-energy electron diffraction (LEED)	Electrons	Electrons
High resolution e^- E loss spec. (HREELS)	Electrons	Electrons
Rutherford backscattering (RBS)	H+ or He+	H+ or He+
Secondary ion mass spec. (SIMS)	Ions	Ions
Laser desorption mass spec. (LDMS)	Photons	Ions

UHV-electrochemistry

Electrochemical X-ray Photoelectron Spectroscopy

Electrochemical XPS

UHV-XPS

Glove Box

***Ex-situ* Analysis without Contamination**

Mass spectrometry

Differential electrochemical mass spectrometry (DEMS)

DEMS: fuel cell catalysts for methanol(solid) & formic acid(dotted) oxidation

Quartz crystal microbalance

QCM: PVF on Au

X-ray methods
Synchrotron

X-ray absorption spectroscopy

Absorption edge (energy that is just needed to eject a particular core electron, e.g., 1s e^- (K edge), $2p_{3/2}$ e^- (L_3 edge)

Fe & Fe oxides
K-edge: 7.112 keV

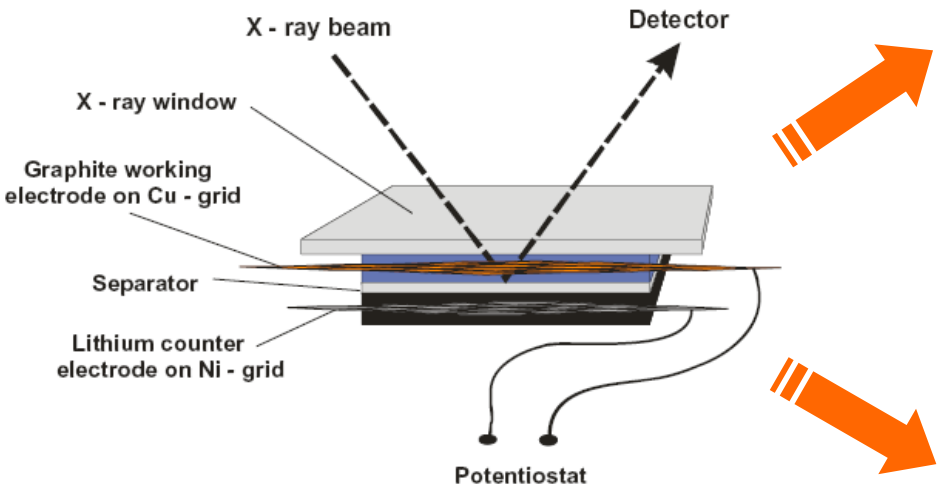
Within 10-40 eV: X-ray absorption near-edge structure (**XANES**) (or near-edge absorption fine structure (**NEXAFS**))
→ oxidation state & ligand envirionment

About 50 keV: extended X-ray absorption Fine structure (**EXAFS**)
→ distance & arrangement of atoms

X-ray diffraction techniques

In situ XRD

Schematic of in situ XRD cell



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전기화학 및 in situ 장비교육 강좌/실습 제공!!