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Characterization methods of inorganic materials

X-ray photoelectron spectroscopy (XPS)

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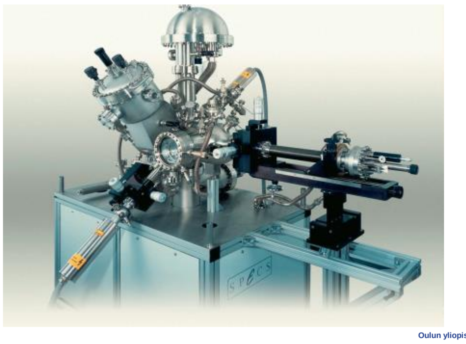


Goals of this lecture

To learn the basic principles of X-ray photoelectron spectroscopy (XPS)

- What can be measured?
- How can it be measured?

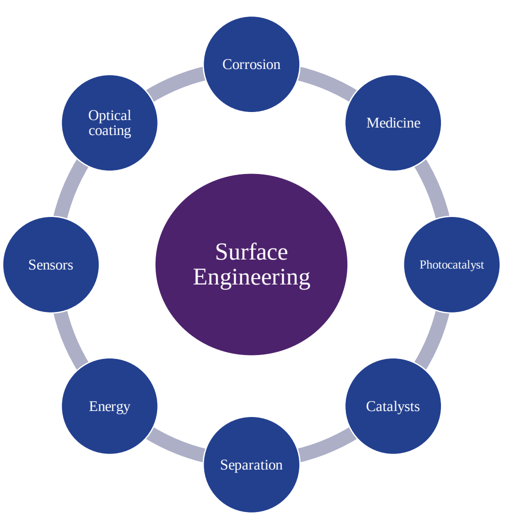
To learn about the types of data that can be obtained from XPS spectra

- Elemental analysis
- oxidation states of elements
- Qualiative
- Quantiative
- State-of-the-art examples

Content

- Introduction
- Instrumentation and basic principles
- Theory and basis
- Database
- XPS applications and examples
- XPS analysis comparison
- XPS pros and cons
- Summary
- References

Introduction



The *surface chemistry* plays a pivotal role in chemical reactions and materials properties

- Gas-solid or liquid-solid reactions or mass transfer
- Thin film technologies (CVD, PVD)
- Corrosion is surface phenomenon
- Adhesive materials (polymers)

Ambient circumstances highly affect the surface characteristics

- Temperature, pH, external fields, photons and radiations

Understanding the mechanism of a particular surface phenomenon will help to improve the efficiency of the process

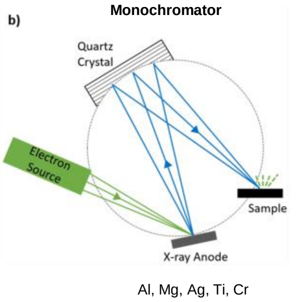
Introduction

Surface characterization analysis methods:

Elemental analysis
- Secondary-Ion Mass Spectroscopy (**SIMS**)
- Auger Electron Spectroscopy (**AES**)
- X-ray Photoelectron Spectroscopy (**XPS**)

Topographic analysis
- Scanning Tunneling Microscope (**STM**)
- Atomic Force Microscopy (**AFM**)
- Magnetic Force Microscopy (**MFM**)
- Lateral Force Microscopy (**LFM**)

XPS Instrumentation and basic principles



Al, Mg, Ag, Ti, Cr

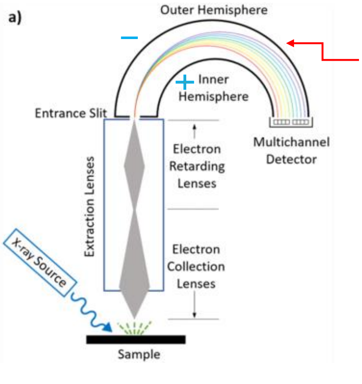


TABLE 3.3 Pressure Range Definitions as Used by AVS in Units of Pascal (the SI Unit for Pressure) and Torr (See Table 3.1 for Conversion Factors)

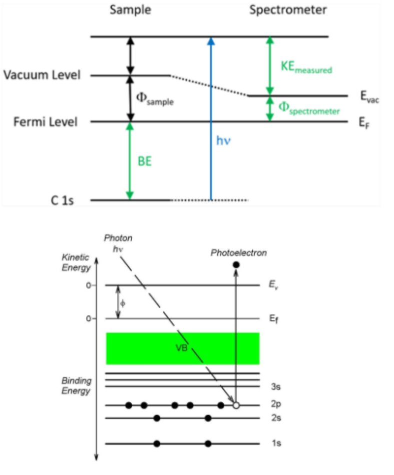
Nomenclature	Pressure (Pa)	Pressure (Torr)
Low vacuum (LV)	$1 \times 10^5 \leftrightarrow 3.3 \times 10^3$	$760 \leftrightarrow 25$
Medium vacuum (MV)	$3 \times 10^3 \leftrightarrow 1 \times 10^{-1}$	$25 \leftrightarrow \sim 1 \times 10^{-3}$
High vacuum (HV)	$1 \times 10^{-1} \leftrightarrow 1 \times 10^{-4}$	$\sim 1 \times 10^{-3} \leftrightarrow 1 \times 10^{-6}$
Very high vacuum (VHV)	$1 \times 10^{-4} \leftrightarrow 1 \times 10^{-7}$	$\sim 1 \times 10^{-6} \leftrightarrow 1 \times 10^{-9}$
Ultrahigh vacuum (UHV)	$1 \times 10^{-7} \leftrightarrow 1 \times 10^{-10}$	$\sim 1 \times 10^{-9} \leftrightarrow 1 \times 10^{-12}$
Extremely high vacuum (XHV)	$<1 \times 10^{-10}$	$<\sim 1 \times 10^{-12}$

Diffraction order	X-ray line	Energy (eV)
1	AlKα	1486.6
2	AgLα	2984.3
3	TiKα	4510.0
4	CrKβ	5946.7

Images from Stevie, Fred A., and Carrie L. Donley. "Introduction to x-ray photoelectron spectroscopy." Journal of Vacuum Science & Technology A 38.6 (2020).

Tables from Watts, John F., and John Wolstenholme. An introduction to surface analysis by XPS and AES. John Wiley & Sons, 2019. & Van der Heide, Paul. X-ray photoelectron spectroscopy: an introduction to principles and practices. John Wiley & Sons, 2011.

XPS Theory and basis



$$h\nu = BE + KE + \Phi_{spec}.$$

$$BE = h\nu - KE - \Phi_{spec}.$$

Where:

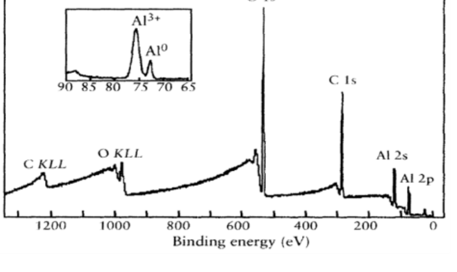
hv: The X-ray energy

BE: The binding energy (how tightly it is bound to the atom/orbital to which it is attached)

KE: Kinetic energy (KE) of the electron that is emitted

Φ: Work function of the spectrometer which is the amount of energy absorbed by the instrument by moving photoelectron from solid state sample to the vacuum chamber (constant value)

XPS Theory and basis

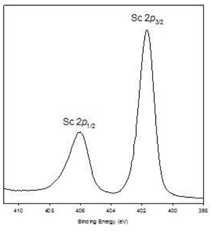


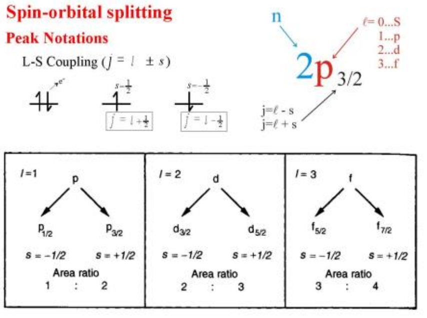
Source of image and data from XPS analysis lecture (2020) by Prof. Mir ghasem Hosseini and Dr. Mahdi Ebrahimi Farshchi at university of Tabriz

What kinds of peaks can be obtained from XPS spectra?

- Sharp peaks (elastically scattered from first layers)
- Spin orbit splitting
- Multiplet splitting (occurs when unpaired electrons exist)
- Satellite peaks (Shake up, Shake off)
- Plasmon
- Overlapping peaks
- Chemical Shifts (Due to atomic interactions and oxidation)
- Auger peaks

XPS Theory and basis



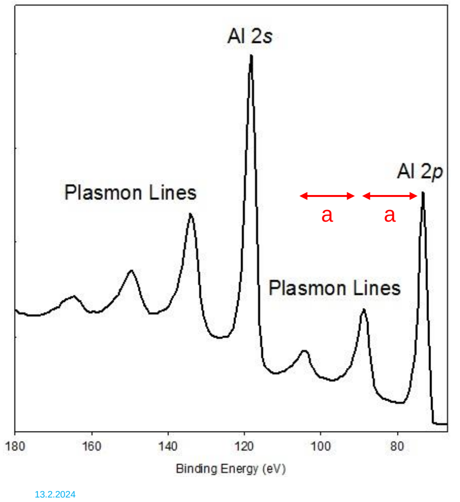


$m(j)=2j+1$

Spin-orbital splitting peaks

- Spin orbital coupling describes the process of an interaction between unpaired electron (with spin 'S') and its electronic orbital (orbital angular momentum 'L')
- S orbitals don't show splitting peaks
- The Total angular momentum 'j' is calculated as $j= l \pm S$

XPS Theory and basis



Plasmon peaks

- Specific to clean metal surfaces
- Photoelectron excites collective oscillations in the conduction band (free electron)
- Photoelectron interact with surface plasmons
- Discrete energy loss (higher binding energies)

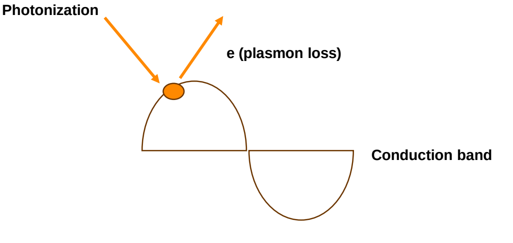
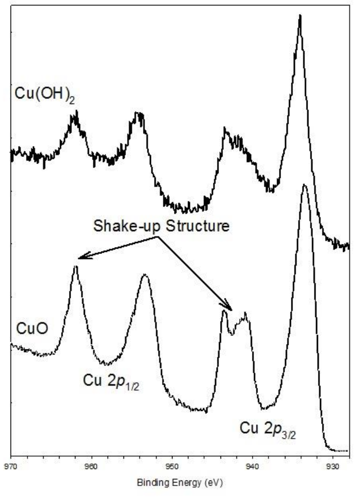


Image from http://www.xpsfitting.com/2012/08/plasmon-loss.html

XPS Theory and basis



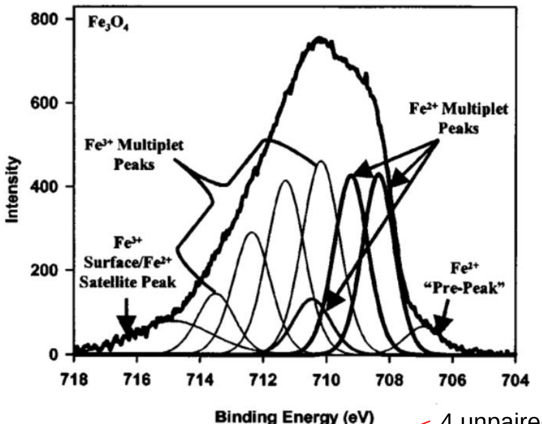
Satellite peaks (Shake-up and Shake-off)

- Non-monochromator
- Shake-up results from a de-excitation process, where the outgoing core electron interacts with a valence electron and excites it to a higher energy level and as a results its kinetic energy decreases and small peaks appear at higher binding energies.
- If the valance electron is ejected completely, a broadening will appear in core level peak (Shake-off)
- The strength and shape of the shake-up features can aid in the assignment of chemical states

Image from M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, *Appl. Surf. Sci.* **257** (2010) 887.

XPS Theory and basis

Multiplet splitting



4 unpaired electrons

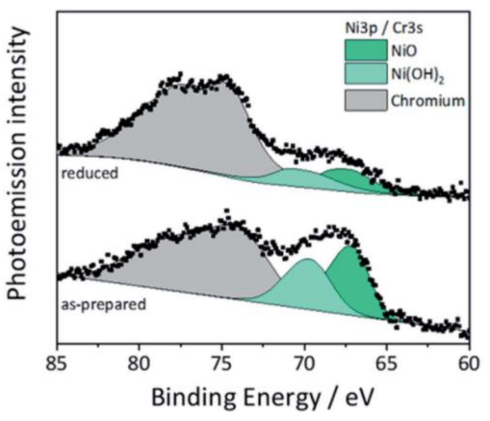
Fe: [Ar] $3d^6 4s^2$

- When a core electron vacancy is made, there can be coupling between the unpaired electron in the core with the unpaired electrons in the outer shell.
- This affects the s orbitals of some transition metals [Mn(II), Cr(II), Cr(III), Fe(III)] and can be observed for some p and d orbitals as well.
- Curve fitting is carried out by Gaussian, Lorentzian, Voigt and Pseudo-Voigt mathematical models*

Image from https://xpslibrary.com/multiplet-splitting-2p-cr-mn-fe-co-ni/
***Source:** Major, George H., et al. "Practical guide for curve fitting in x-ray photoelectron spectroscopy." Journal of Vacuum Science & Technology A 38.6 (2020).

XPS Theory and basis

Overlapping

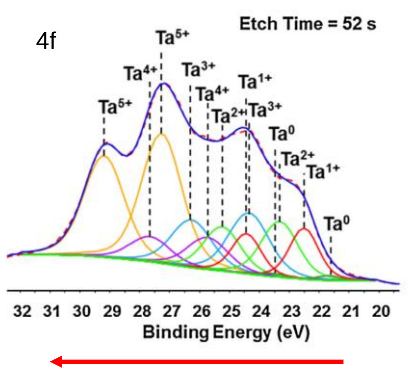


- Occurs when multiple components or different oxidation states coexist in the sample
- Instead of sharp peaks a wider peak is displayed.

Image from Amaya-Dueñas, Diana-María, et al. "A-site deficient chromite with in situ Ni exsolution as a fuel electrode for solid oxide cells (SOCs)." Journal of Materials Chemistry A 9.9 (2021): 5685-5701.

XPS Theory and basis

Chemical shifts



Ta_2O_5, TaO_2, Ta_2O_3, TaO, Ta_2O

- Atoms of a higher positive oxidation state exhibit a higher binding energy due to the **extra coulombic interaction** between the photo-emitted electron and the ion core.

Functional Group		*Binding Energy (eV)*	
hydrocarbon	C-H, C-C	285.0	C — Electronegativity Increase
amine	C-N	286.0	N
alcohol, ether	C-O-H, C-O-C	286.5	O
Cl bound to C	C-Cl	286.5	Cl — Binding energy increase
F bound to C	C-F	287.8	F
carbonyl	C=O	288.0	Double-bond

Image from Simpson, Robin, et al. "XPS investigation of monatomic and cluster argon ion sputtering of tantalum pentoxide." Applied Surface Science 405 (2017): 79-87.

XPS Theory and basis

Chemical shifts

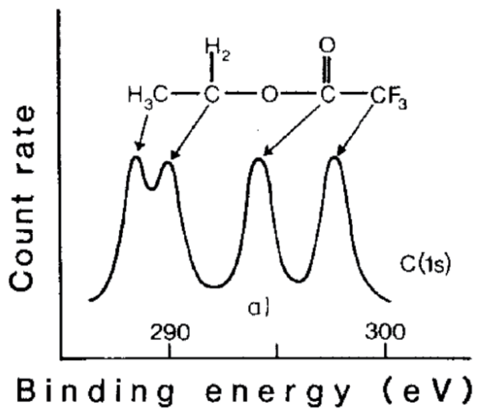


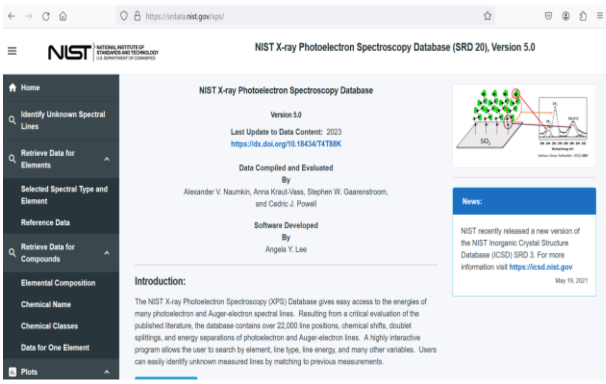
Image from Siegbahn K, N.C., Fahlman A, Hamrin H, Hedman J, Johansson G, Bergmark T, Karlsson S E, Lindgren J and Lindberg B: 'Electron Spectroscopy for Chemical Analysis. Atomic, Molecular and Solid State Structure Studies by Means of Electron Spectroscopy' (1967. 1967)

XPS Database

Element	1s	2s	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
H (H_2 gas)	13.6								
He (He gas)	24.6*								
Li	54.7*								
Be	111.5*								
B	188*								
C (graphite)	284.7[b]								
N (N_2 gas)	409.9*	37.3*							
N (ionic solid)	399.0[b]	12.0[b]							
O (O_2 gas)	543.1*	41.6*							
O (ionic solid)	531.0[b]	22.0[b]							
F (F_2 gas)	696.7*	—							
F (ionic solid)	686.0[b]	31.0[b]							
Ne (Ne gas)	870.2*	48.5*	21.7*	21.6*					
Na	1070.8†	63.5†	30.81[a]	30.65[a]					
Mg	1303.0†	88.7	49.78	49.50					
Al	1559.6	117.8	72.95	72.55					
Si	1839	149.7*[a]	99.82	99.42					
P	2145.5	189*	136*	135*					
S	2472	230.9	163.6*	162.5*					
Cl (Cl_2 gas)	2822.4	270*	202*	201*					
Cl (ionic solid)	—	270[b]	202[b]	200[b]					
Ar (Ar gas)	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*		
K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*		
Ca	4038.5*	438.4†	349.7†	346.2†	44.3†	25.4†	25.4†		
Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*		
Ti	4,966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†		
V	5,465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†		
Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†		
Mn	6539	769.1†	649.4†	638.7†	82.3†	47.2†	47.2†		

Table from Van der Heide, Paul. X-ray photoelectron spectroscopy: an introduction to principles and practices. John Wiley & Sons, 2011.

XPS Database



NIST X-ray Photoelectron Spectroscopy Database

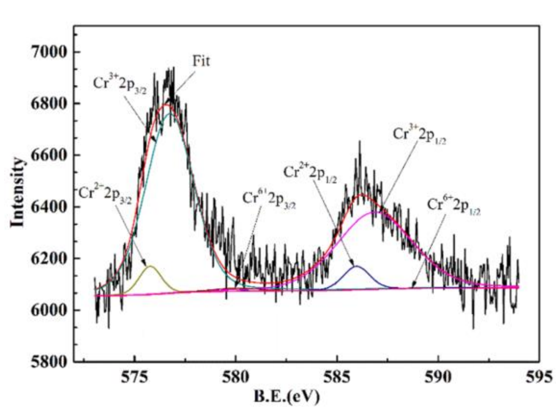
- https://srdata.nist.gov/xps
- http://www.lasurface.com/database/

Softwares

- CasaXPS
- XPSpeak41

XPS Applications and Examples

Determination of chromium valence state in the CaO–SiO2–FeO–MgO–CrOx system by XPS

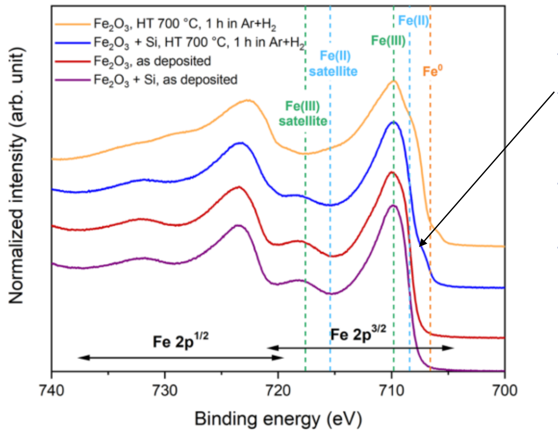


- Effect of Oxygen on the valence state of chromium
- Effect of basicity on the valence state of chromium
- Effect of Cr2O3 on the valence state of chromium
- Effect of temperature on the valence state of chromium
- More than 77.99% Cr is trivalent Cr(III). The fraction of Cr(II)/Cr is in the range of 11.24–17.22%. The fraction of Cr(VI)/Cr is below 4.80%.

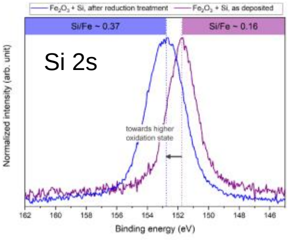
Source: Liu, Deman, et al. "Determination of chromium valence state in the CaO–SiO2–FeO–MgO–CrO x system by X-ray photoelectron spectroscopy." *High Temperature Materials and Processes* 39.1 (2020): 351-356.

XPS Applications and Examples

Effect of Si on the hydrogen-based direct reduction of Fe2O3 studied by XPS of sputter-deposited thin-film model systems



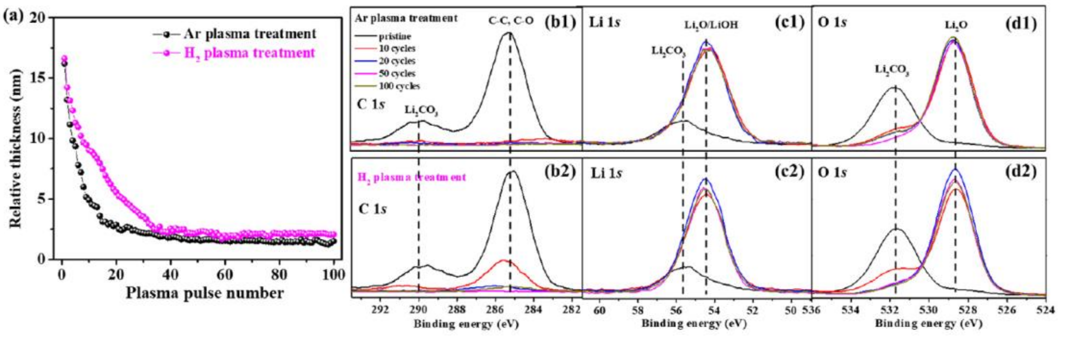
- Si doped Fe2O3 thin film has less reduction efficiency
- Fe(II) signal in blue line has a chemical shift of -0.5 eV of wustite 2p3/2 spectra, which represents Fe2SiO4 (not wustite)
- Fe(III) satellite peaks are disappeared, and Fe(II) satellite peaks are appeared in the yellow line
- Si enrichment on the surface



Source: Patterer, Lena, et al. "Effect of Si on the hydrogen-based direct reduction of Fe2O3 studied by XPS of sputter-deposited thin-film model systems." Scripta Materialia 233 (2023): 115515.

XPS Applications and Examples

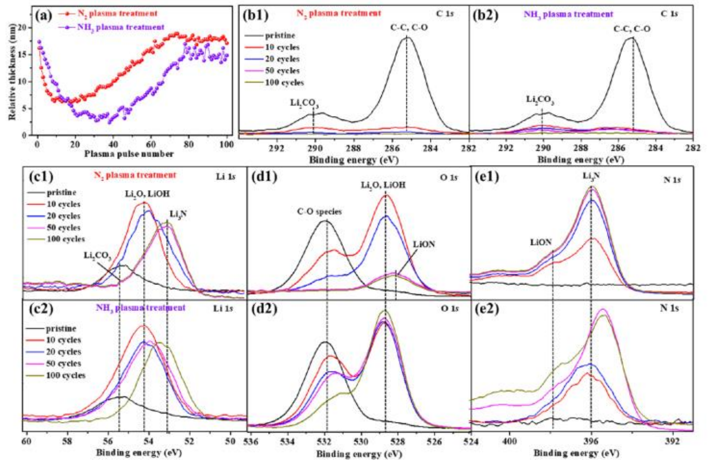
In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment



Source: Zhao, Bo, et al. "In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment." Journal of Energy Chemistry 66 (2022): 295-305.

XPS Applications and Examples

In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment



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XPS Applications and Examples

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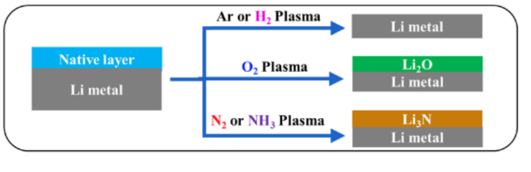

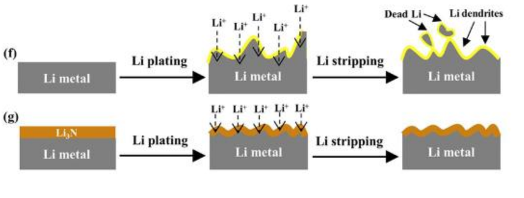

- A clean metallic Li surface could be obtained after Ar plasma or H_2 plasma treatments.
- Plasma treatment eliminates unwanted carbonaceous species.
- Passivated Li_3N layer exhibits high stability and mitigates the growth of Li dendrites during charge-discharge process.

Source: Zhao, Bo, et al. "In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment." Journal of Energy Chemistry 66 (2022): 295-305.

XPS analysis comparison with other surface analysis methods

Table 6.1 Features of various analytical methods discussed in the text

	Incident radiation	Emitted radiation	Property monitored	Elements detectable	Depth of analysis	Spatial resolution	Information level E = elemental C = chemical	Quantification*	Applicability to inorganics*	Applicability to organics*
AES	e^-	e^-	Energy	Li on	3–10 nm	<12 nm	E (C)	✓	0	X
EDX	e^-	X-ray	Energy	Be on	1 µm	1 µm	E	✓	0†	X†
EELS	e^-	e^-	Energy	Li on	Depends on foil thickness	10 nm	E	0	✓	X
ISS	ions	ions	Energy	Li on	Outer atom layer	100 µm	E	0	✓	0
LAMMS	laser	ions	Mass	All	0.5 µm	1 µm	E, C	X	✓	✓
RBS	ions	ions	Energy	Li on	1 µm	1 mm	E	X	✓	✓‡
SIMS (static)	ions	ions	Mass	All	1.5 nm	1 µm	C (E)	X	✓	✓
SIMS (dynamic)	ions	ions	Mass	All	See text	50 µm	E	0	✓	X
SIMS (imaging)	ions	ions	Mass	All	See text	50 nm	C (E)	X	0	0
XPS	X-rays	e	Energy	He on	3–10 nm	STD 1 mm^2 small area: 10 µm imaging XPS: <3 µm	E, C	✓	✓	✓

*✓ = very good, 0 = reasonable, X = poor
†Without conductive coating
‡Cryo-stage required

Tables from Watts, John F., and John Wolstenholme. An introduction to surface analysis by XPS and AES. John Wiley & Sons, 2019. & Van der Heide, Paul. X-ray photoelectron spectroscopy: an introduction to principles and practices. John Wiley & Sons, 2011.

XPS analysis pros and cons

Advantages	Disadvantages
Nondestructive	No bulk state information
Surface sensitive (10-200 Å)	Expensive ($200,000-$500,000/ instrument, $50-$500/ sample)
Elemental sensitivity (parts per 1000)	High vacuum (10^-8 to 10^-11 torr)
All elements (except H and He)	Slow (1/2 to 8 hours/sample)
Quantitative	Charging and energy referencing can be a problem
Chemical bonding information	Low resolution (-0.1-1.0 eV)

Source: Andrade, Joseph D. "X-ray photoelectron spectroscopy (XPS)." Surface and Interfacial Aspects of Biomedical Polymers: Volume 1 Surface Chemistry and Physics (1985): 105-195.

Summary

XPS is among the most powerful surface analysis methods, which can provide the following information:

- Elements on the surface and their chemical states
- Oxide-reduced states of metals
- Qualitative information
- Quantitative information
- Mechanistic studies
- Depth-profiling (3-10 nm)

A comprehensive database is available, but practical experience is needed to avoid misleading information from the fitted curves.

References

[1] Watts, John F., and John Wolstenholme. An introduction to surface analysis by XPS and AES.

[2] John Wiley & Sons, 2019. & Van der Heide, Paul. X-ray photoelectron spectroscopy: an introduction to principles and practices. John Wiley & Sons, 2011.

[3] Stevie, Fred A., and Carrie L. Donley. "Introduction to x-ray photoelectron spectroscopy." Journal of Vacuum Science & Technology A 38.6 (2020).

[4] Major, George H., et al. "Practical guide for curve fitting in x-ray photoelectron spectroscopy." Journal of Vacuum Science & Technology A 38.6 (2020).

[5] Liu, Deman, et al. "Determination of chromium valence state in the CaO–SiO2–FeO–MgO–CrO x system by X-ray photoelectron spectroscopy." High Temperature Materials and Processes 39.1 (2020): 351-356.

[6] Patterer, Lena, et al. "Effect of Si on the hydrogen-based direct reduction of Fe2O3 studied by XPS of sputter-deposited thin-film model systems." Scripta Materialia 233 (2023): 115515.

[7] Zhao, Bo, et al. "In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment." Journal of Energy Chemistry 66 (2022): 295-305.

[8] Andrade, Joseph D. "X-ray photoelectron spectroscopy (XPS)." Surface and Interfacial Aspects of Biomedical Polymers: Volume 1 Surface Chemistry and Physics (1985): 105-195.

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