Ambient pressure x-ray photoemission and absorption spectroscopies

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Lecture outlook

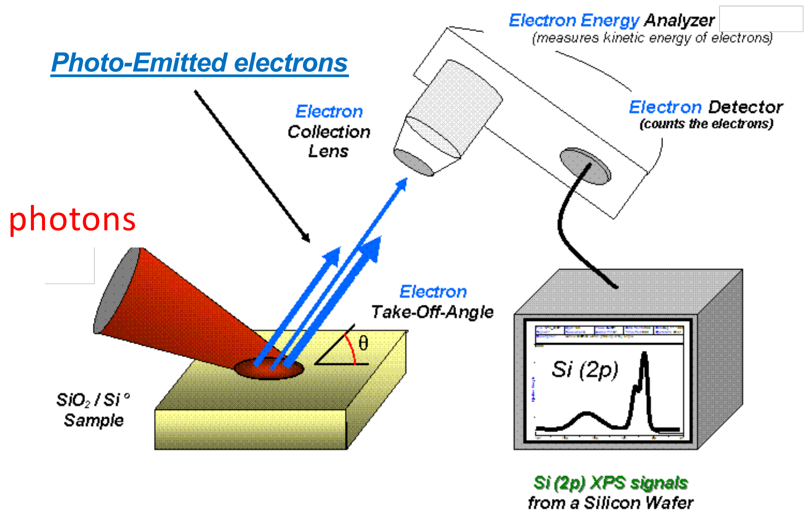
- what is XPS (quick intro)
- e-spectrometer: how it works
- NAP-XPS
-AP-NEXAFS
-Instrument
-examples

PhotoElectron Spectroscopy (PES) or X-ray Photoemission Spectroscopy (XPS)

Photoelectron Spectroscopy (PES) is a widely used technique to investigate the chemical composition of surfaces.

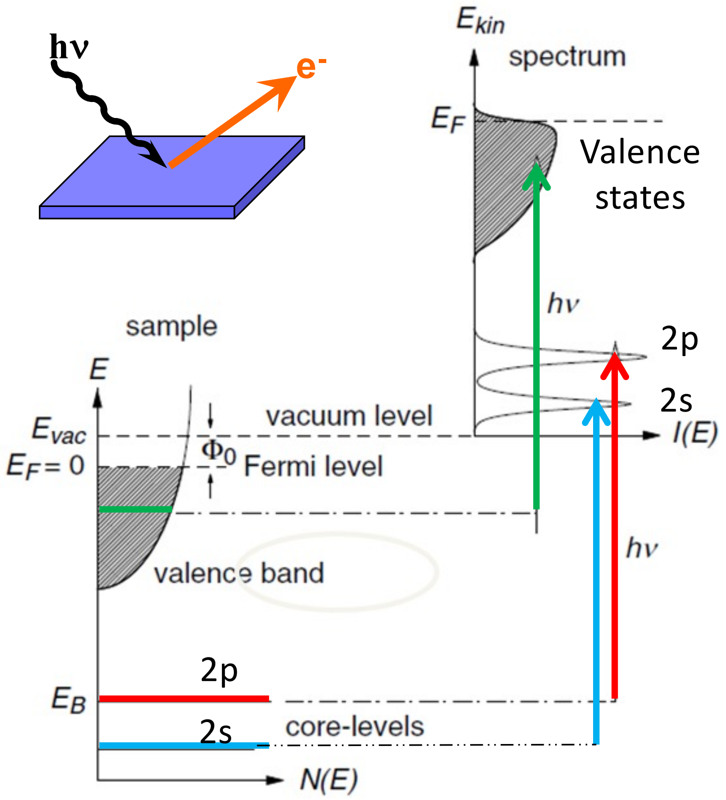
"What is?"	*Elemental composition*
"How much is?"	*Quantitative analysis*

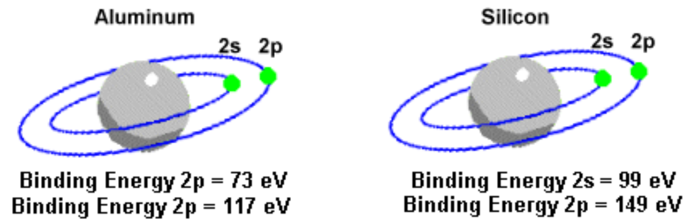
PES can probe many features of the electronic structure, thus providing information useful for the comprehension e.g. of spin/charge transport, magnetic properties, local structural order, etc…



- *Irradiate a solid with monoenergetic UV/X-ray radiation*
- *Analyze the energies of the emitted electrons*

Photoelectric effect





$$E_K = h\nu - E_B - \phi_{AN}$$

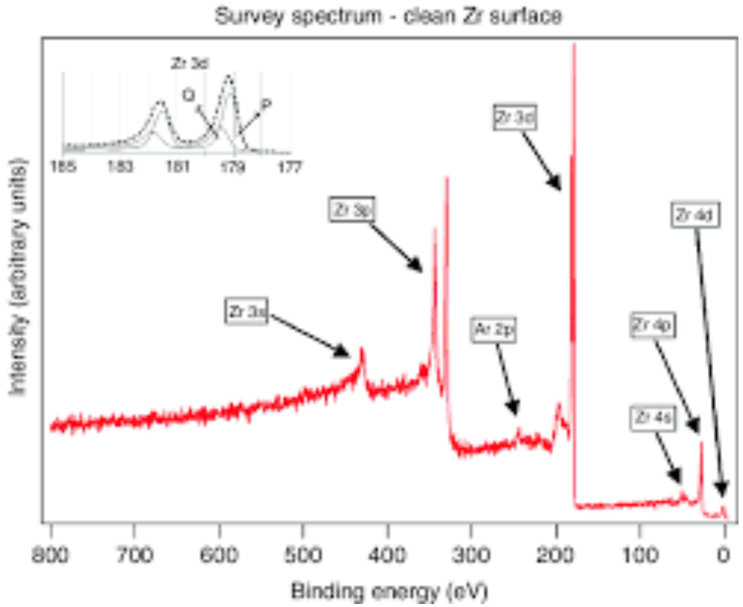
$h\nu$: photon energy

E_B : core level binding energy

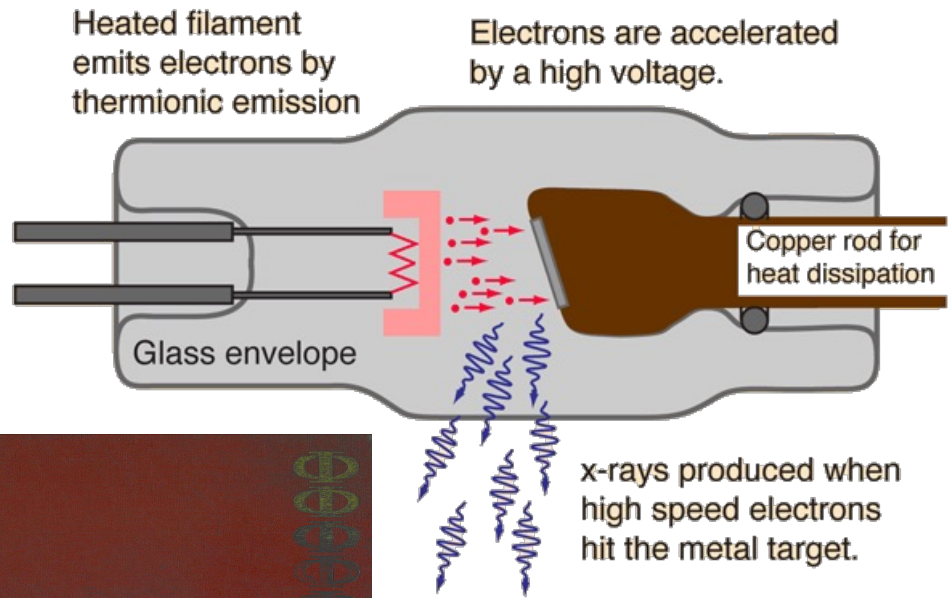
ϕ_{AN}: work function of the electron analyzer

1. H. Hertz, Ann. Physik 31,983 (1887).
2. A. Einstein, Ann. Physik 17,132 (1905). 1921 Nobel Prize in Physics.
3. K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

Standard XPS: chemical analysis with laboratory sources



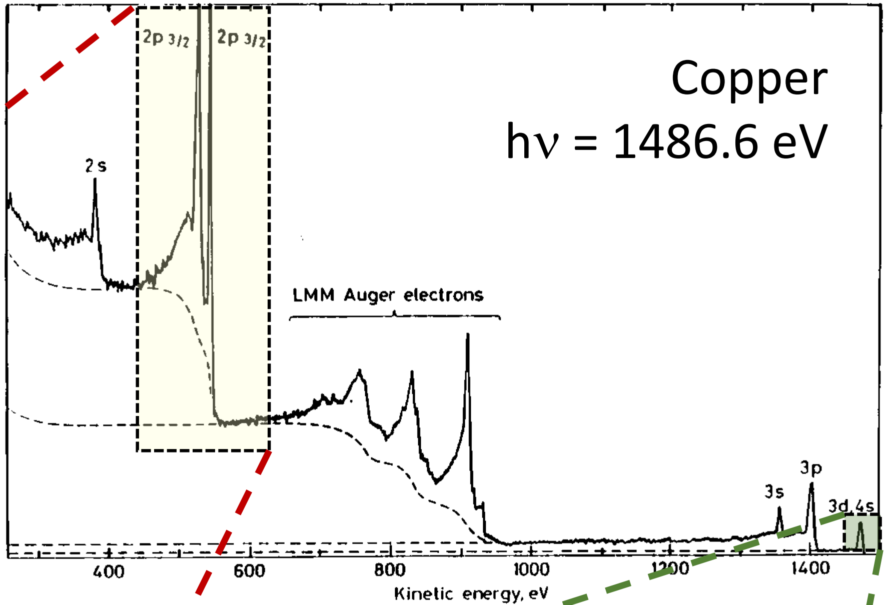
X ray tube



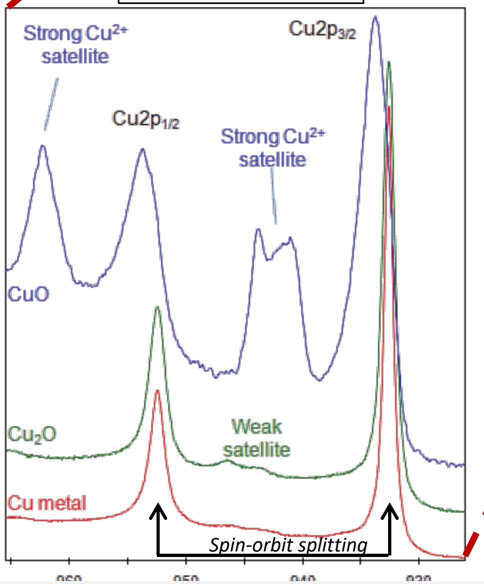
Reference: handbook of x ray photoemission spectroscopy

CHEMICAL STATE SENSITIVITY

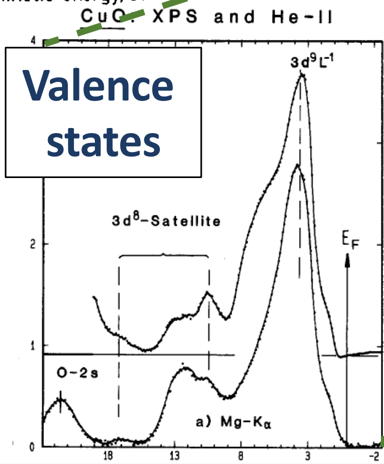
Core level spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).



Core levels

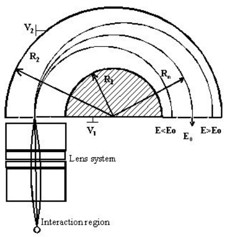


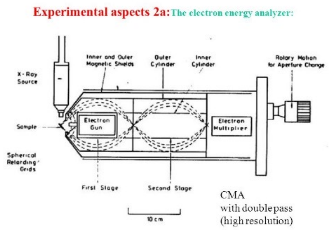
Valence states



Electron energy analysers

Electrostatic energy analyser

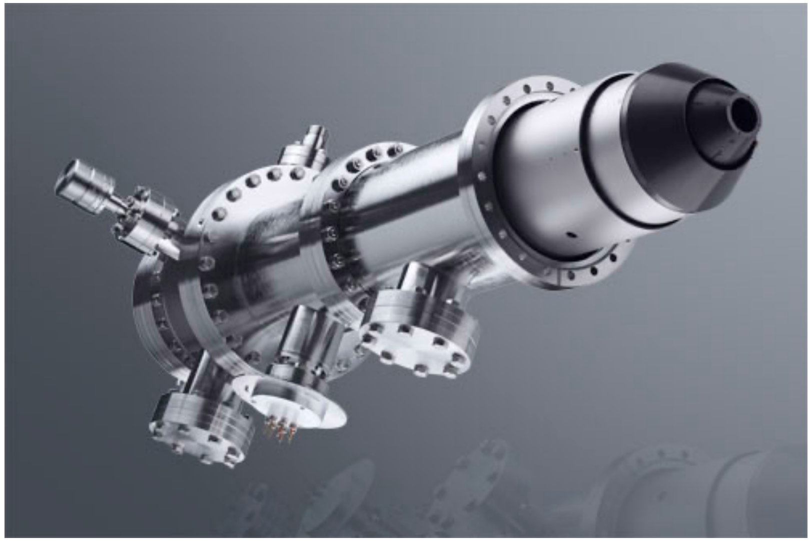




Hemispherical or cilindrical

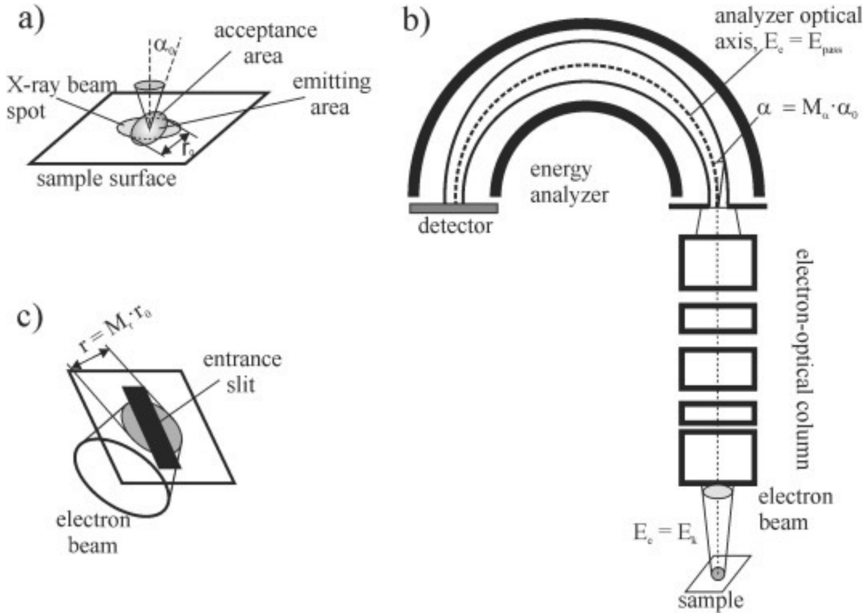
Broad application field with standard and synchrotron sources

Time of flight



Require pulsed sources, special applications:
Time resolved experiment
Angular resolved photoemission

The king of analysers: electrostatic hemispherical analyser

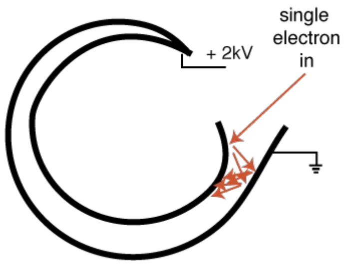


Mean radius: 150 mm

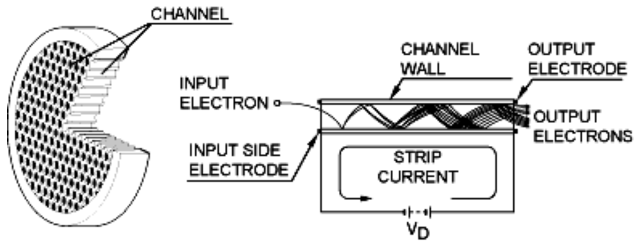
3 (4) parts: input lenses
hemisphers
detectors

Detectors: electron multipliers

Channeltrons



Microchannel plate



Both require vacuum better than 10-6 mbar!!!

The pressure gap: bridging the distance between UHV and real world

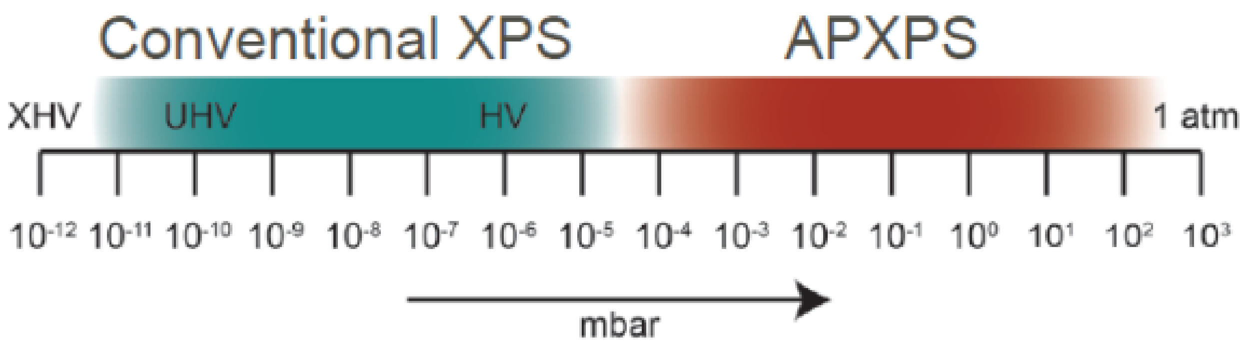
To gain inside in the catalitic processes we need to apply the spectroscopic analysis to real processes…

NAP-XPS

AP_XAS in the soft x ray

Development of electron based **operando** spectroscopies

Ambient pressure XPS

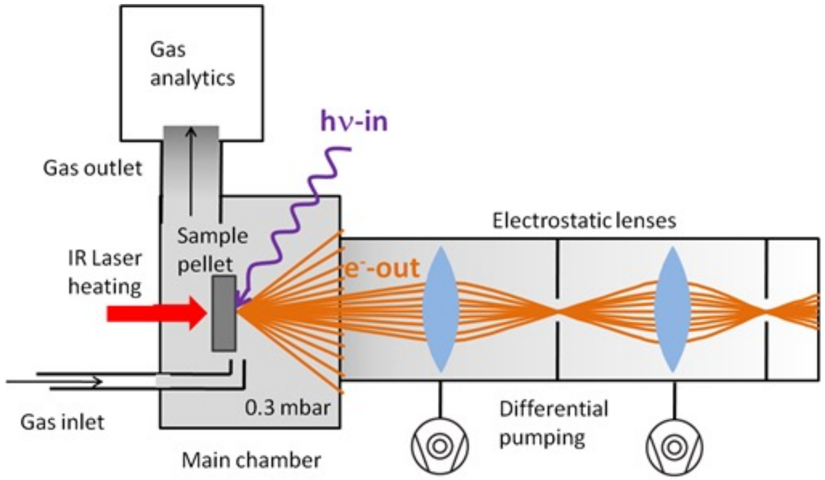


Motivation:
-surface structure may differ from what observed in UHV
-Dynamic effect can play a significant role
-Dynamic processes may be studied
-Material with high vapor pressure can be studied

Problems:
1) Electron analyser require UHV

2) Electron escape depth

Analyser for NAP-XPS (a smart solution…)



Several differential pumping stages

Extremely expensive, brute force…………

Input lenses focalize electron in small apertures to help differential pumping

NAP-XPS experimental setups

ALS
Brookhaven

Bessy II (3)
Diamond
Max4 (2)
SLS
SOLEIL
Elettra2.0

Pohang (SK)
NSLS
Shangai
Photon Factory
Nanoterasu

Benchmark experiment: chemical reactivity @ surfaces

ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

Ambient-Pressure X-ray Photoelectron Spectroscopy Study of Cobalt Foil Model Catalyst under CO, H_2, and Their Mixtures

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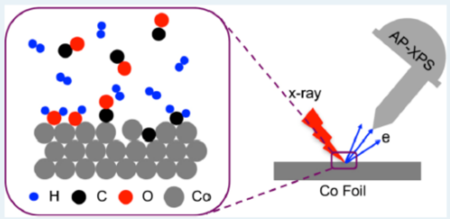
Supporting Information

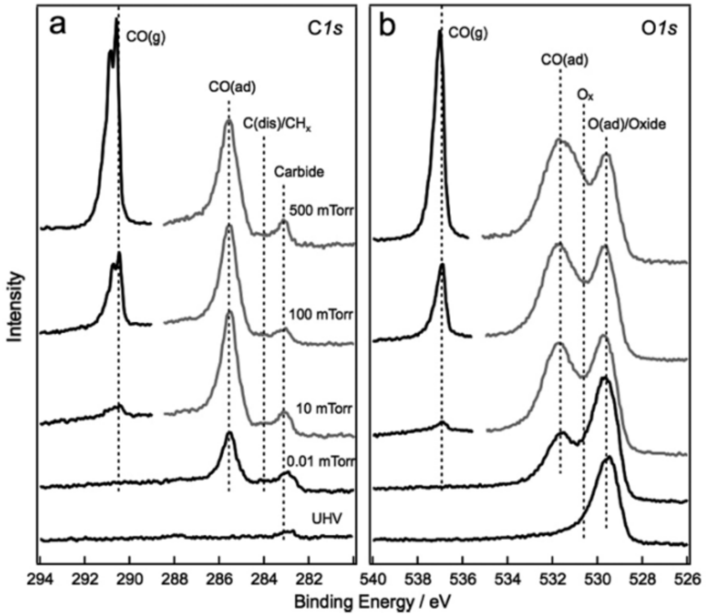
ABSTRACT: Ambient-pressure X-ray photoelectron spectroscopy (XPS) was used to investigate the reactions of CO, H_2, and their mixtures on Co foils. We found that CO adsorbs molecularly on the clean Co surface and desorbs intact in vacuum with increasing rate until ~90 °C where all CO desorbs in seconds. In equilibrium with 100 mTorr gas, CO dissociates above 120 °C, leaving carbide species on the surface but no oxides, because CO efficiently reduces the oxides at temperatures ~100 °C lower than H_2. Water as impurities or produced by reaction of CO and H_2 efficiently oxidizes Co even at room temperature. Under 97:3 CO/H_2 mixture and with increasing temperatures, the Co surface becomes more oxidized and covered by hydroxyl groups until ~150 °C where surface starts to get reduced, accompanied by carbide accumulation indicative of CO dissociation. A similar trend was observed for 9:1 and 1:1 mixtures, but surface reduction begins at higher temperatures.



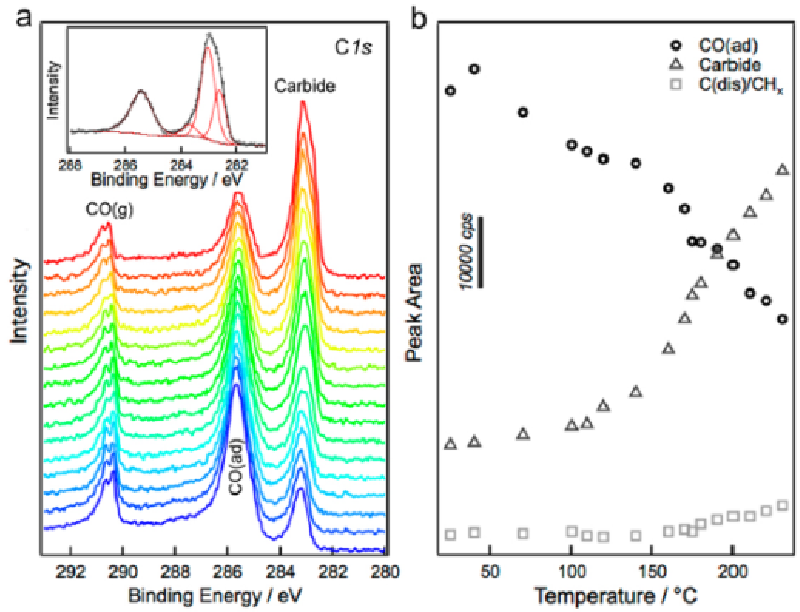
KEYWORDS: *catalysis, Fischer–Tropsch synthesis, cobalt, ambient-pressure X-ray photoelectron spectroscopy*

ACS Catal. 2017 72 1150-1157

The classical experiment NAP-XPS



As a function of P



As a function of T

Example 2: solid/liquid interfaces

SCIENTIFIC REPORTS

OPEN

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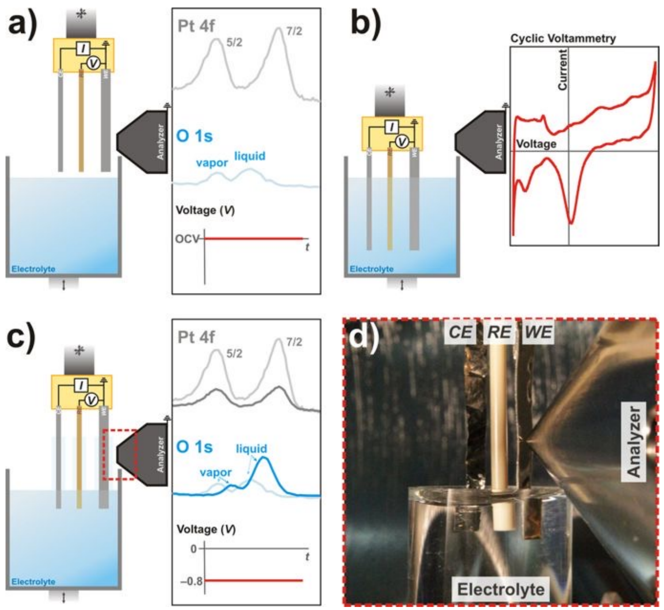
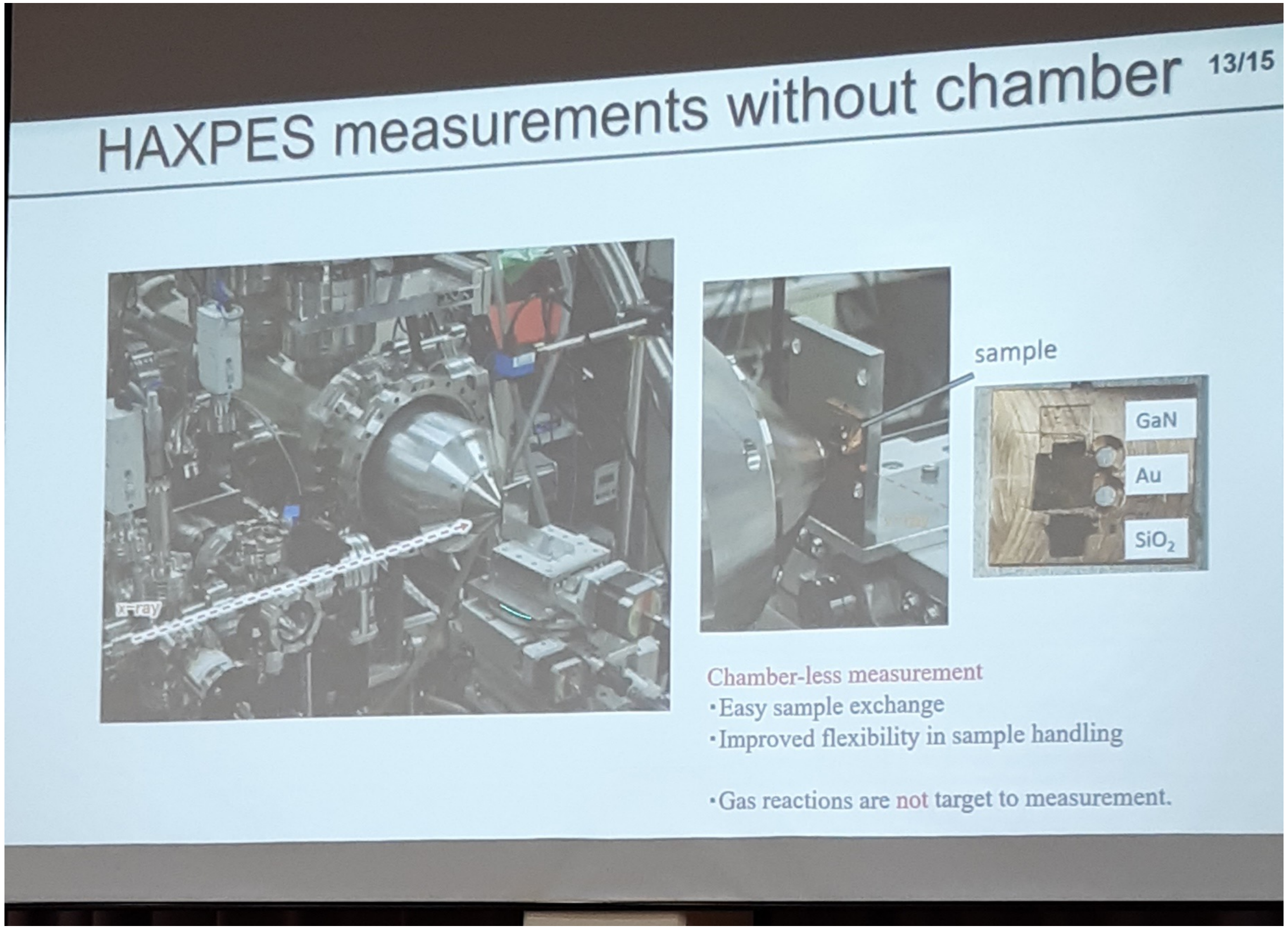
Using "Tender" X-ray Ambient Pressure X-Ray Photoelectron Spectroscopy as A Direct Probe of Solid-Liquid Interface

Stephanus Axnanda[1,#], Ethan J. Crumlin[1,#], Baohua Mao[1,2], Sana Rani[1], Rui Chang[1,2], Patrik G. Karlsson[3], Mårten O. M. Edwards[3], Måns Lundqvist[3], Robert Moberg[3], Phil Ross[4], Zahid Hussain[1] & Zhi Liu[1,2,5]

We report a new method to probe the solid-liquid interface through the use of a thin liquid layer on a solid surface. An ambient pressure XPS (AP-XPS) endstation that is capable of detecting high kinetic energy photoelectrons (7 keV) at a pressure up to 110 Torr has been constructed and commissioned. Additionally, we have deployed a "dip & pull" method to create a stable nanometers-thick aqueous electrolyte on platinum working electrode surface. Combining the newly constructed AP-XPS system, "dip & pull" approach, with a "tender" X-ray synchrotron source (2 keV–7 keV), we are able to access the interface between liquid and solid dense phases with photoelectrons and directly probe important phenomena occurring at the narrow solid-liquid interface region in an electrochemical system. Using this approach, we have performed electrochemical oxidation of the Pt electrode at an oxygen evolution reaction (OER) potential. Under this potential, we observe the formation of both Pt^{2+} and Pt^{4+} interfacial species on the Pt working electrode *in situ*. We believe this thin-film approach and the use of "tender" AP-XPS highlighted in this study is an innovative new approach to probe this key solid-liquid interface region of electrochemistry.



The last frontier…….



Different approach: membranes!

Atmospheric pressure X-ray photoelectron spectroscopy apparatus: Bridging the pressure gap

J. J. Velasco-Vélez,[1,2,a)] V. Pfeifer,[2] M. Hävecker,[1,a)] R. Wang,[3] A. Centeno,[4] A. Zurutuza,[4] G. Algara-Siller,[2] E. Stotz,[2] K. Skorupska,[1] D. Teschner,[2] P. Kube,[2] P. Braeuninger-Weimer,[3] S. Hofmann,[3] R. Schlögl,[1,2] and A. Knop-Gericke[2]
[1]*Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr 45470, Germany*
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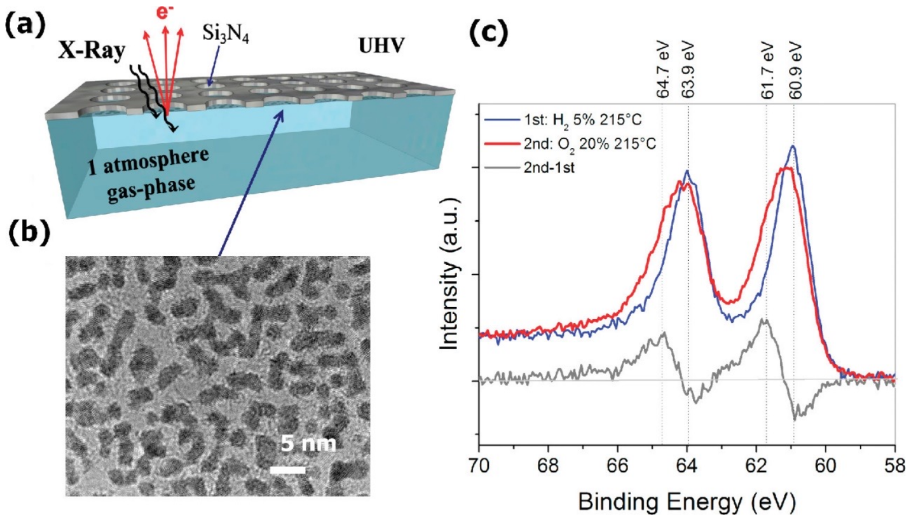
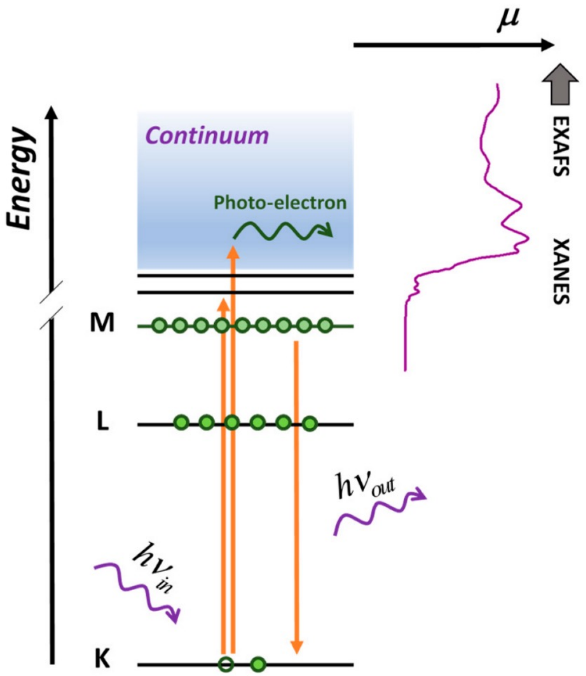
One of the main goals in catalysis is the characterization of solid/gas interfaces in a reaction environment. The electronic structure and chemical composition of surfaces become heavily influenced by the surrounding environment. However, the lack of surface sensitive techniques that are able to monitor these modifications under high pressure conditions hinders the understanding of such processes. This limitation is known throughout the community as the "pressure gap." We have developed a novel experimental setup that provides chemical information on a molecular level under atmospheric pressure and in presence of reactive gases and at elevated temperatures. This approach is based on separating the vacuum environment from the high-pressure environment by a silicon nitride grid—that contains an array of micrometer-sized holes—coated with a bilayer of graphene. Using this configuration, we have investigated the local electronic structure of catalysts by means of photoelectron spectroscopy and in presence of gases at 1 atm. The reaction products were monitored online by mass spectrometry and gas chromatography. The successful operation of this setup was demonstrated with three different examples: the oxidation/reduction reaction of iridium (noble metal) and copper (transition metal) nanoparticles and with the hydrogenation of propyne on Pd black catalyst (powder). *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4951724]



Review of Scientific Instruments **87**, 053121 (2016)

Questions?

Ambient Pressure soft-XAS for solid/gas interfaces



EXAFS

Radial distribution
of neighbours
Crystal structure

NEXAFS
(XANES)

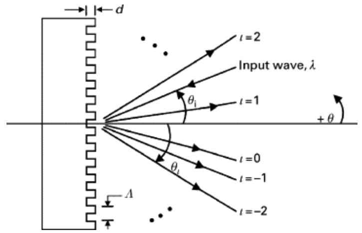
DOS empty states
Electronic
Properties
Oxidation state

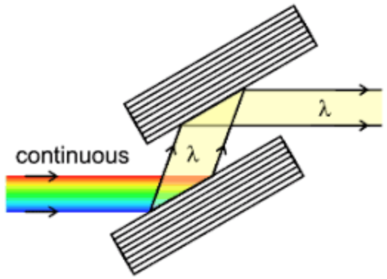
Soft x ray

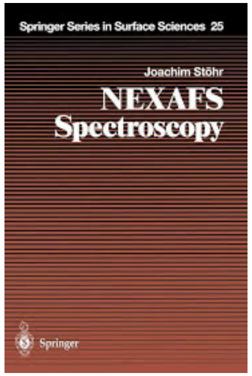
0-2 keV

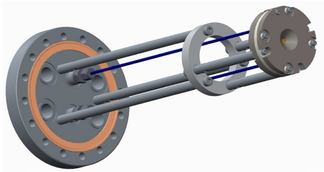
Hard x ray

> 3 keV





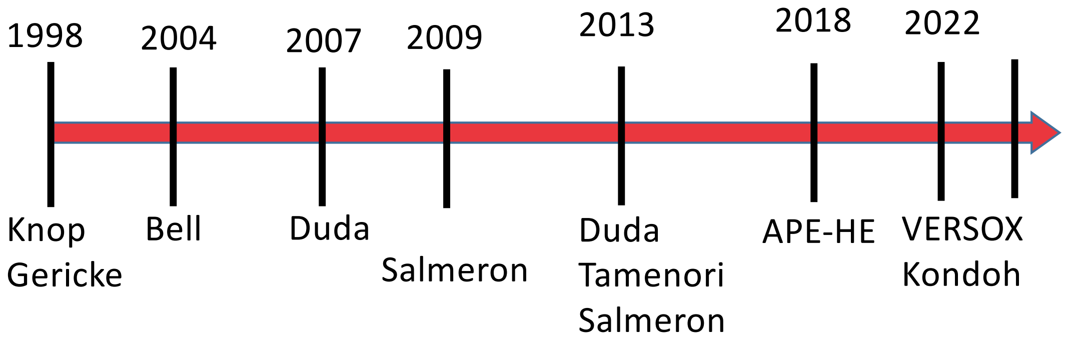




NEXAFS

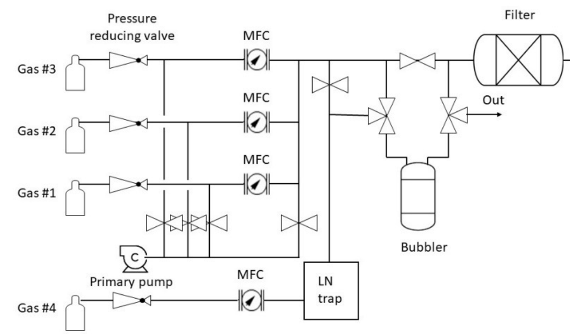
AP soft XAS: brief history

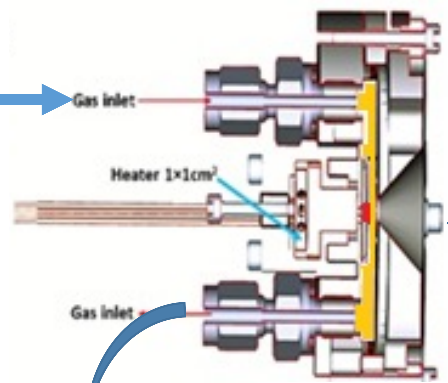
Timeline



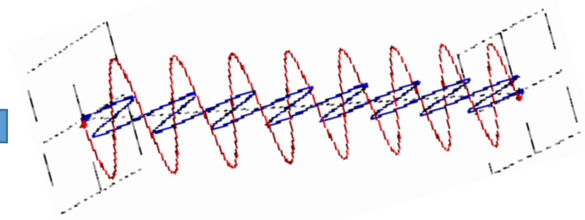
Dedicated Beamlines:
ALS (2?)
Bessy II
Diamond
Elettra
Instruments:
SSLS
Photon Factory (2022)

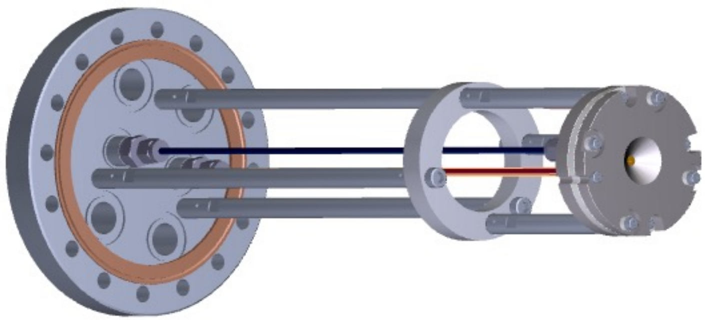
AP Soft-XAS laboratory @APE-HE



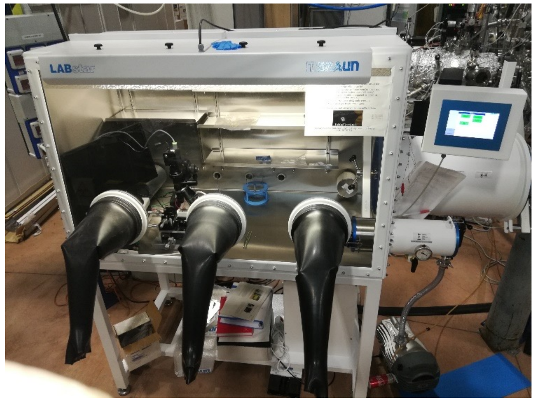


Synchrotron radiation





Micro GC



Benchmark experiment: Solid Oxide Fuel Cells

ACS APPLIED ENERGY MATERIALS

www.acsaem.org Article

Insights into the Redox Behavior of $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$-Derived Perovskites for CO_2 Valorization Technologies

Andrea Felli, Silvia Mauri, Marcello Marelli, Piero Torelli, Alessandro Trovarelli, and Marta Boaro*

Cite This: *ACS Appl. Energy Mater.* 2022, 5, 6687−6699 Read Online

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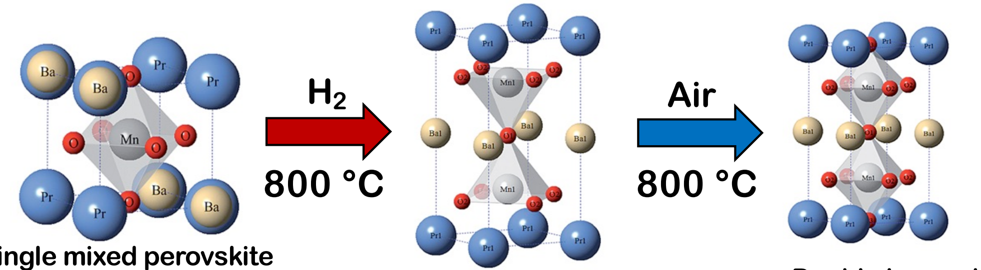
Problem: high working temperature, search for materials that works in intermediate range (400-600 ^{0}C)

PBM Structural properties

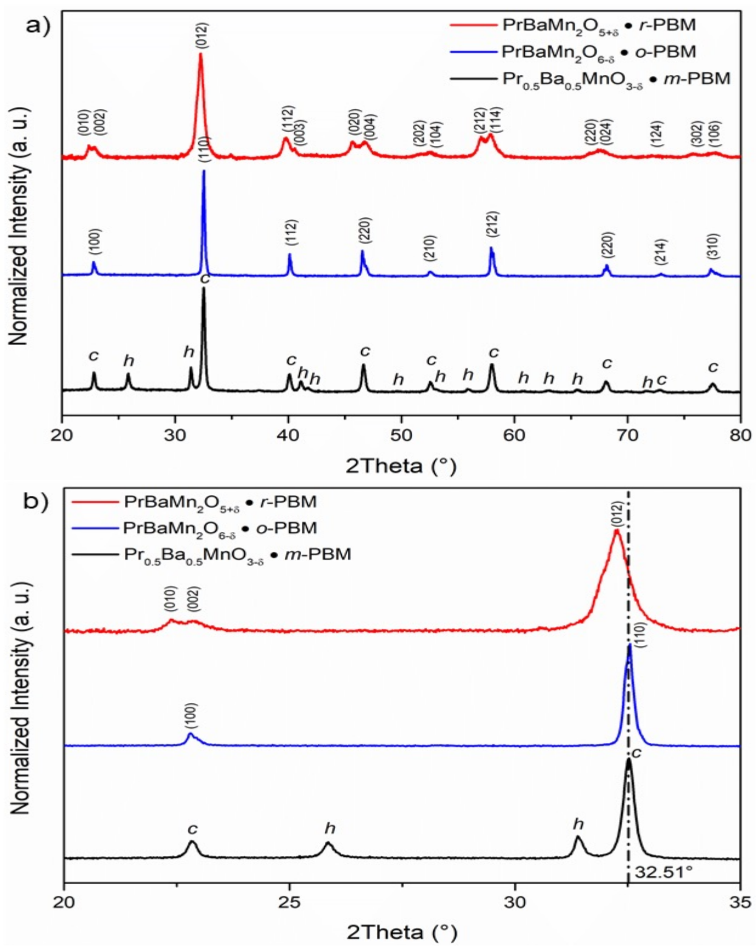


Single mixed perovskite $Pr_{0.5}Ba_{0.5}MnO_{3-\delta}$

T. Shin *et al.*, *Faraday Discuss.*, 2015, 182, 227.

Double layered perovskite $PrBaMn_2O_{5+\delta}$ (r-PBM)

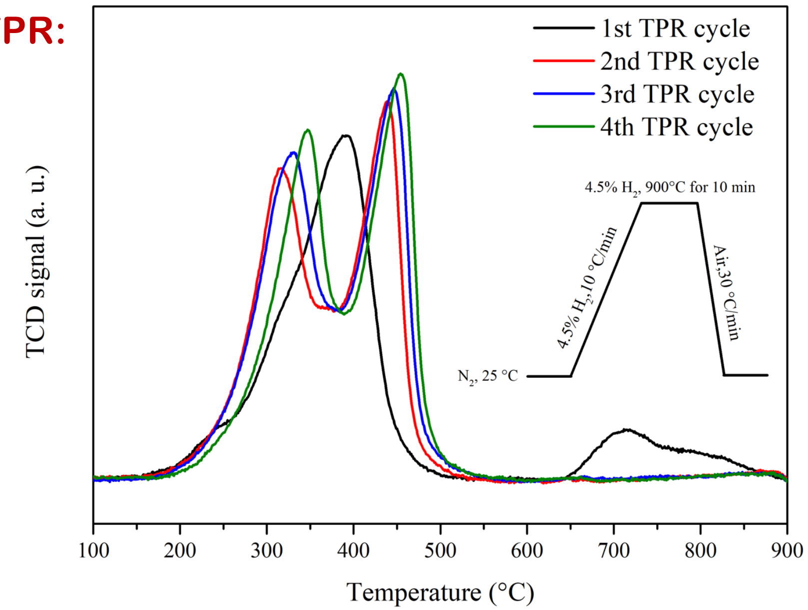
Double layered perovskite $PrBaMn_2O_{6-\delta}$ (o-PBM)



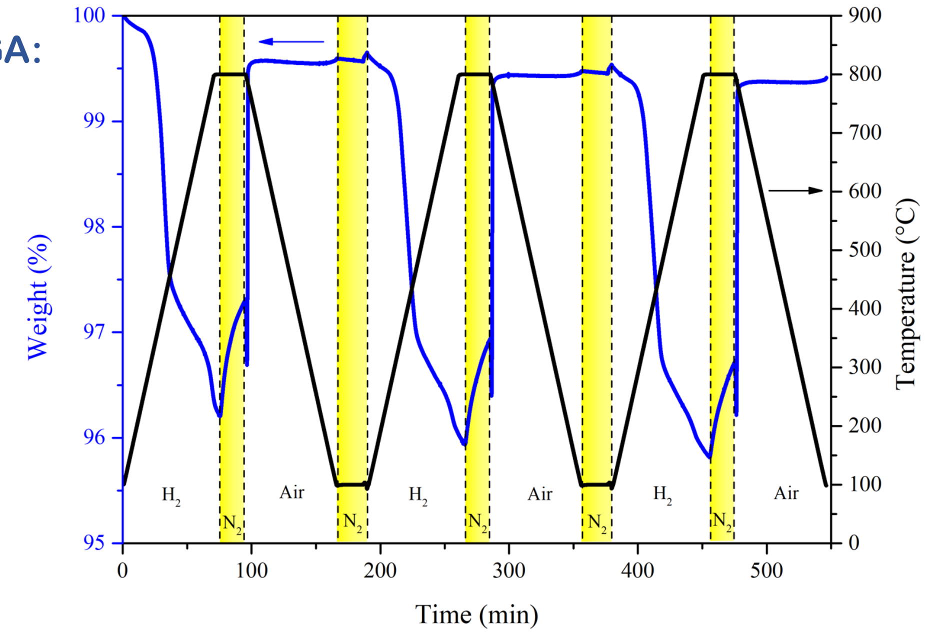
- ✓ **Both high ionic & electronic conductivity;**
- ✓ ***In situ* formation of the layered phase $PrBaMn_2O_{5+\delta}$;**
- ✓ **High stability in reducing environment;**
- ✓ **High sulfur tolerance;**
- ✓ **Good electrochemical activity towards the oxidation of hydrocarbons;**
- ✓ **Employed as electrodes in more advanced technologies (Symmetrical SOFC, Reversible SOC);**
- ✓ **Good matrix for the creation of self-assembled ex-solved nanostructures.**

Redox properties

TPR:



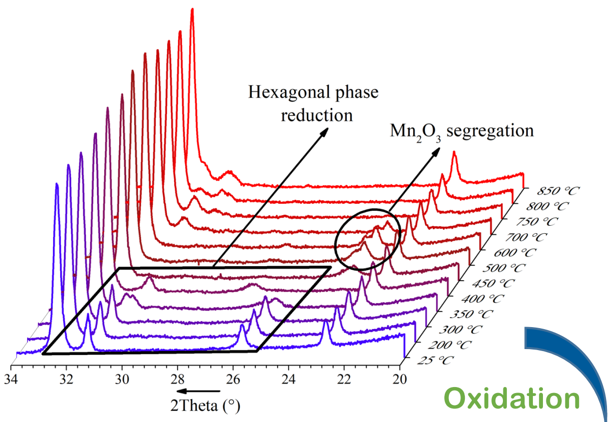
TGA:

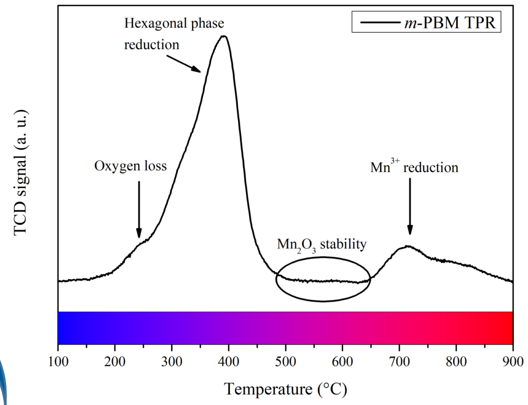


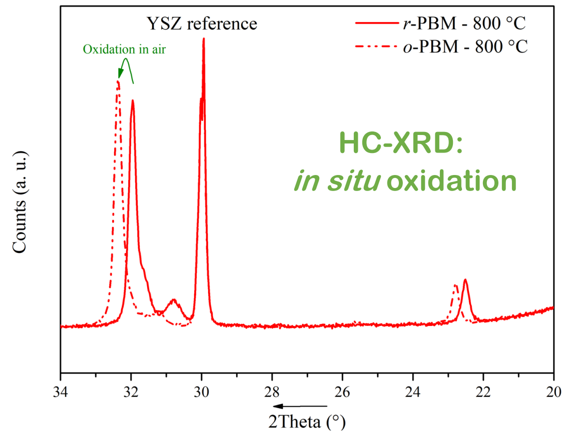
- Splitting of the first consumption peak after the immediate oxidation at high temperature;
- Disappearance of the peak at high temperature;
- Repetition of the TPR signal after every RedOx cycle.

- Same trend after every Redox cycle;
- Immediate re-oxidation of the *r*-PBM phase;
- Results in line with the TPR experiments.

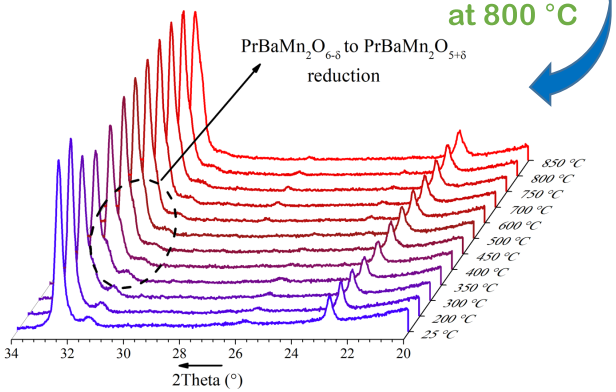
In situ-XRD

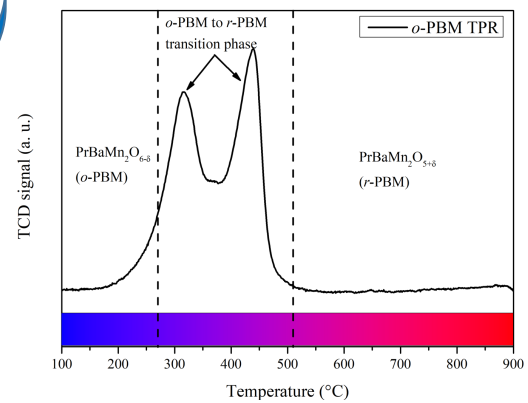


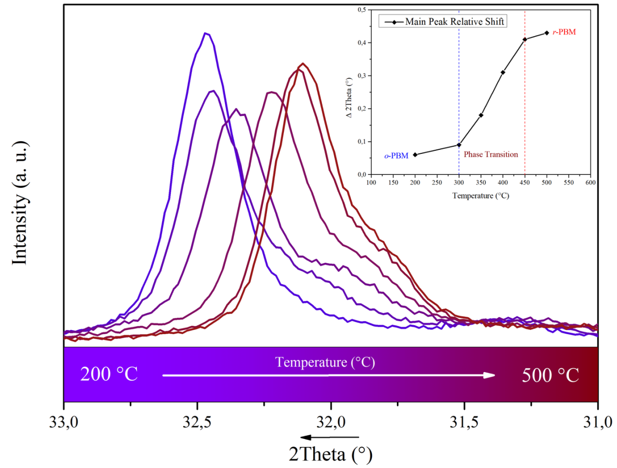




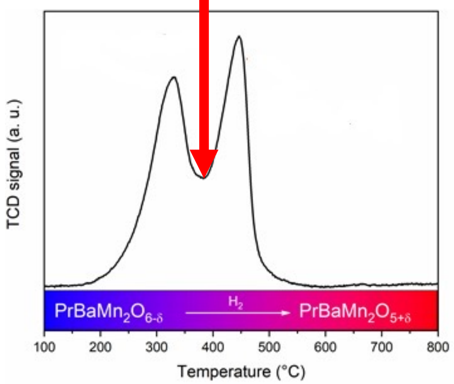
Oxidation at 800 °C



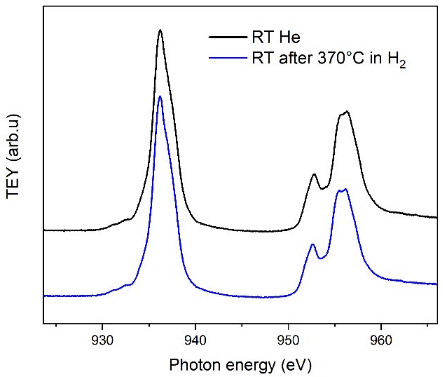




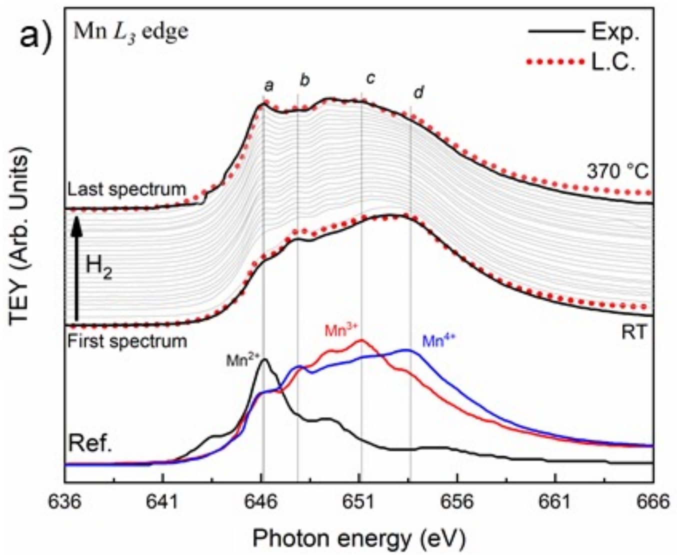
In situ Soft-XAS



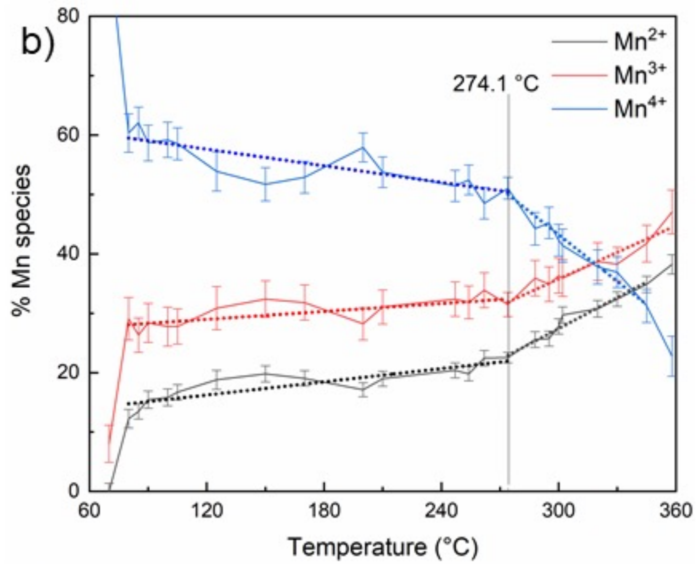
Pr $M_{4,5}$ edges



Pr and BA
do not participate



Linear combination of
Mn reference spectra

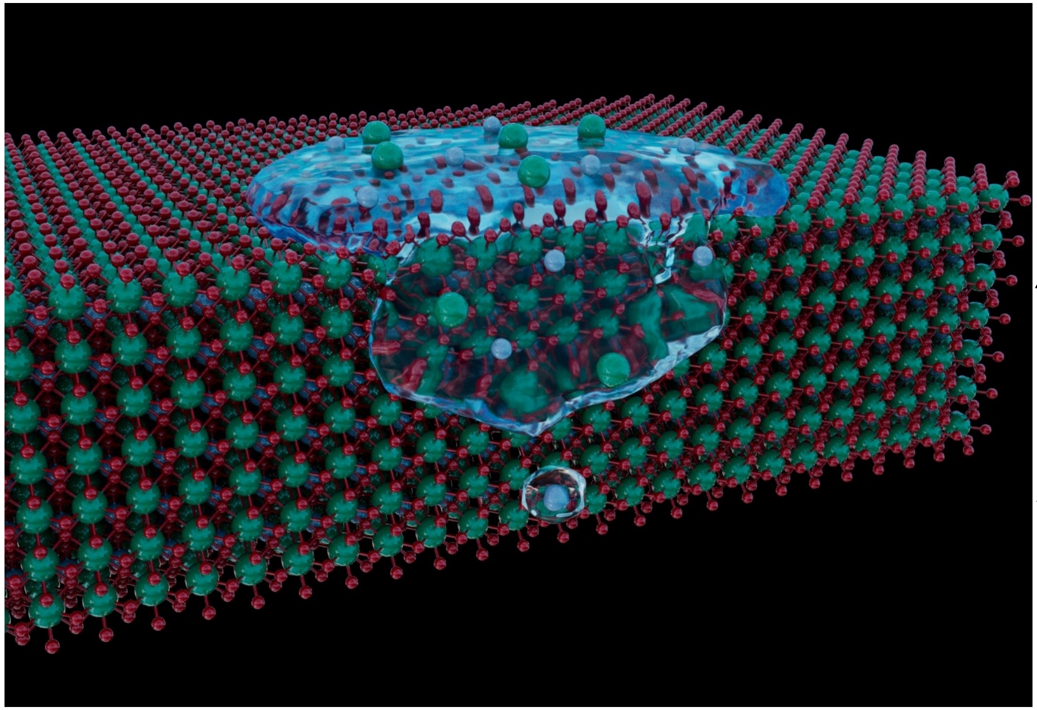


Nominal charge 3.5

Presence of Mn 2+ (surface phase)

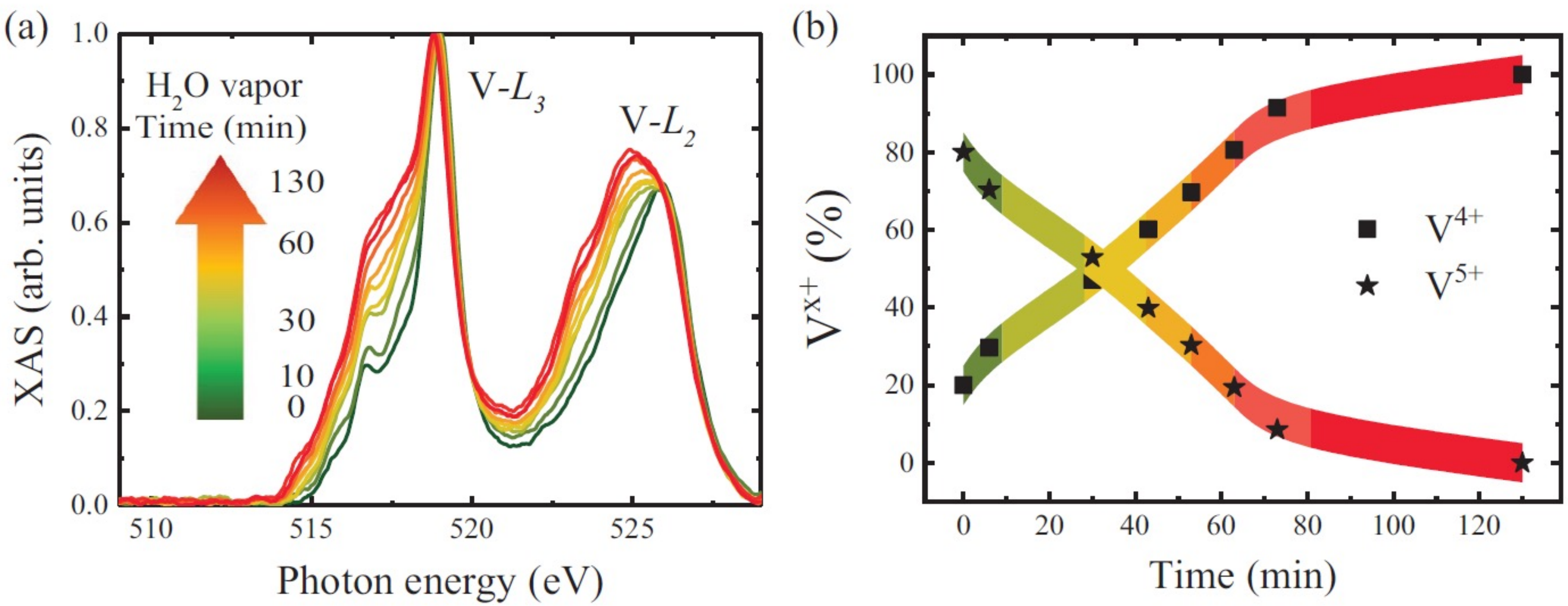
Mn 4+ to Mn 3+ and Mn 2+

Water interaction with surfaces



V. Polewczyk, M. Mezhoud, M. Rath, O. El-Khaloufi, F. Bassato, A. Fouchet, W. Prellier, M. Frégnaux, D. Aureau, L. Braglia, G. Vinai, P. Torelli and U. Lüders, "Formation and Etching of the Insulating Sr-Rich V5+ Phase at the Metallic SrVO3 Surface Revealed by operando XAS Spectroscopy Characterizations ", **Adv. Funct. Mater. 2301056 (2023).**

V reduction under water exposition



Aged SrVO3 present over-oxydized phase at surfaces. Sample has been exposed to 1 Bar of He with 3% of water vapor

Reflectivity measurement and etching

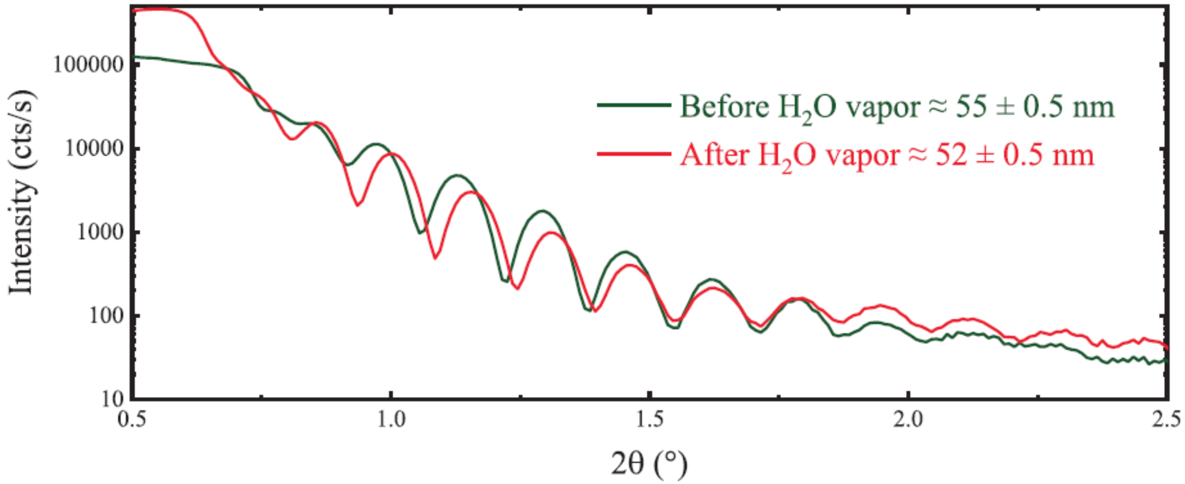


Figure 4. X-ray reflectivity measurements performed on the aged SVO sample before (dark green) and after (red) the water vapor cleaning treatment.

Comparison between NAP-XPS and AP soft-XAS

	NAP-XPS	Soft-XAS
Surface sensitivity	🙂	🙂
Informative	🙂	🙂
Rough condition	☹️	😒
Acquisition time	☹️	🙂
Table of elements	🙂	☹️

Weak point the elements atteinable, however for C,O,N or Transition metals or rare earth is probably more efficient from many point of view.