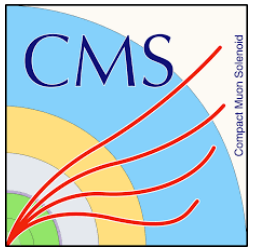
"Aging 2023: 3rd International Conference on Detector Stability and Aging Phenomena in Gaseous Detectors, 6-10 Nov 2023, CERN, Geneva (Switzerland)"



Material analysis of the MWPC electrodes irradiated in longevity tests

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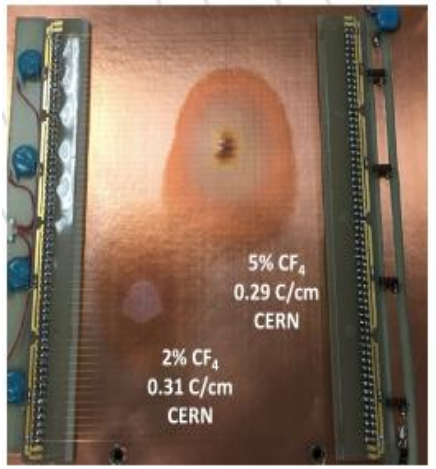
Aging of Multi Wire Proportional Chamber

➢ **Cathode Strip Chamber (CSC)** is Multi Wire Proportional Chamber (MPWC), composed of alternating layers of cathode strip planes and anode wire planes inside a gas volume.

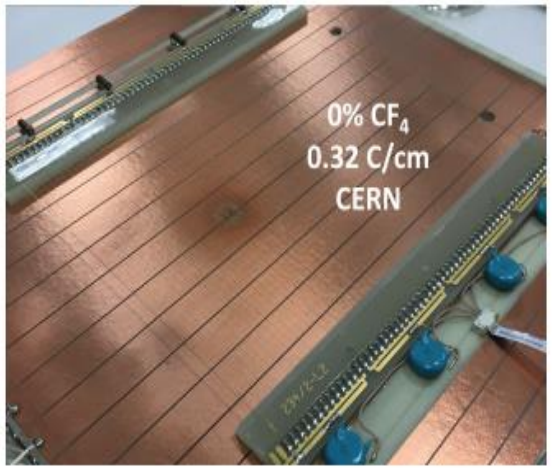
- **Cathode panels:** polycarbonate plates with a honeycomb hexagonal structure fixed between the sheets of **Cu-foil-coated glass-reinforced FR4 plastic** with strips milled into copper.
- **Anode panels: gold-plated tungsten wires**, 50 μm in diameter.

➢ Although, **no signs of CSC detection performance degradation were observed**, except for the HFO tests where dark current increase was detected, visible changes are observed on the electrode surfaces.

MWPC electrodes



Cathode panel



Anode wire panels

Analyzed electrodes

Cathode plates and anode wires from CSC prototypes
Several longevity tests with local irradiation were performed:

- gas mixture 40% Ar + 50% CO_2 + 10% CF_4 , accum. charge ~ 1.3 C/cm *(Physics of Atomic Nuclei, 2019, Vol. 82, No. 9, pp. 1252–1262)*
- gas mixtures 40% Ar + (55-60)% CO_2 + x% CF_4, x = 0, 2 and 5%, accum. charge ~ 0.24 C/cm *(European Physical Journal Plus, accepted)*
- gas mixture 40% Ar + 58% CO_2 + 2% HFO_{1234ze}, accum. charge ~ 1.3 C/cm, HFO_{1234ze} - $C_3H_2F_4$ ($CF_3CH=CHF$) *(Physics of Atomic Nuclei, 2020, Vol. 83, No. 10, pp. 1449–1458)*.

➢ The electrode samples were analyzed at **public funded research facilities in Belgrade**.

Physical and chemical characterization of materials

- Characterization is the application of various analytical techniques in order to fully understand the nature of the material from different aspects. Analytical techniques are used to determine physical and chemical properties of the material – **identify (qualitative) and quantify (amount) chemically, measure physical parameters (electrical properties etc.)**

- Combining various analytical techniques operating at different scales (nano, micro and meso), provide complementary results comprising:

- **surface morphology and roughness**
- **elemental composition**
- **structural information**
  - **middle range ordering at the molecular level (functional groups, e.g. O-H, C-H, etc.)**
  - **long range ordering (crystal or amorphous structure)**

- To determine a degree of deterioration of the electrode's surface (**physical aspect**) and to analyse the deposit formed (**chemical aspect**) in plasma chemical reaction, analytical techniques well established in the field of materials science were used.

Physical and chemical techniques in electrode aging studies

- How are deposits formed on the electrode surfaces
  - products of multiple reactions simultaneously occurring in the avalanche plasma
  - mechanism of deposit formation on the electrodes in such complex system is far from fully understood.

- **Limiting factors** in electrode analysis are **sampling** (cutting of the sample) and **contamination** of the sample during transport, handling and measurements.

- **Systematic effects** cannot be excluded:
  - contamination by carbon (instrument chamber contamination, improper sample handling etc.)
  - to overcome such problems, every measurement of the **aged electrodes was compared to the virgin (reference) electrode** that was not exposed to the process of aging.

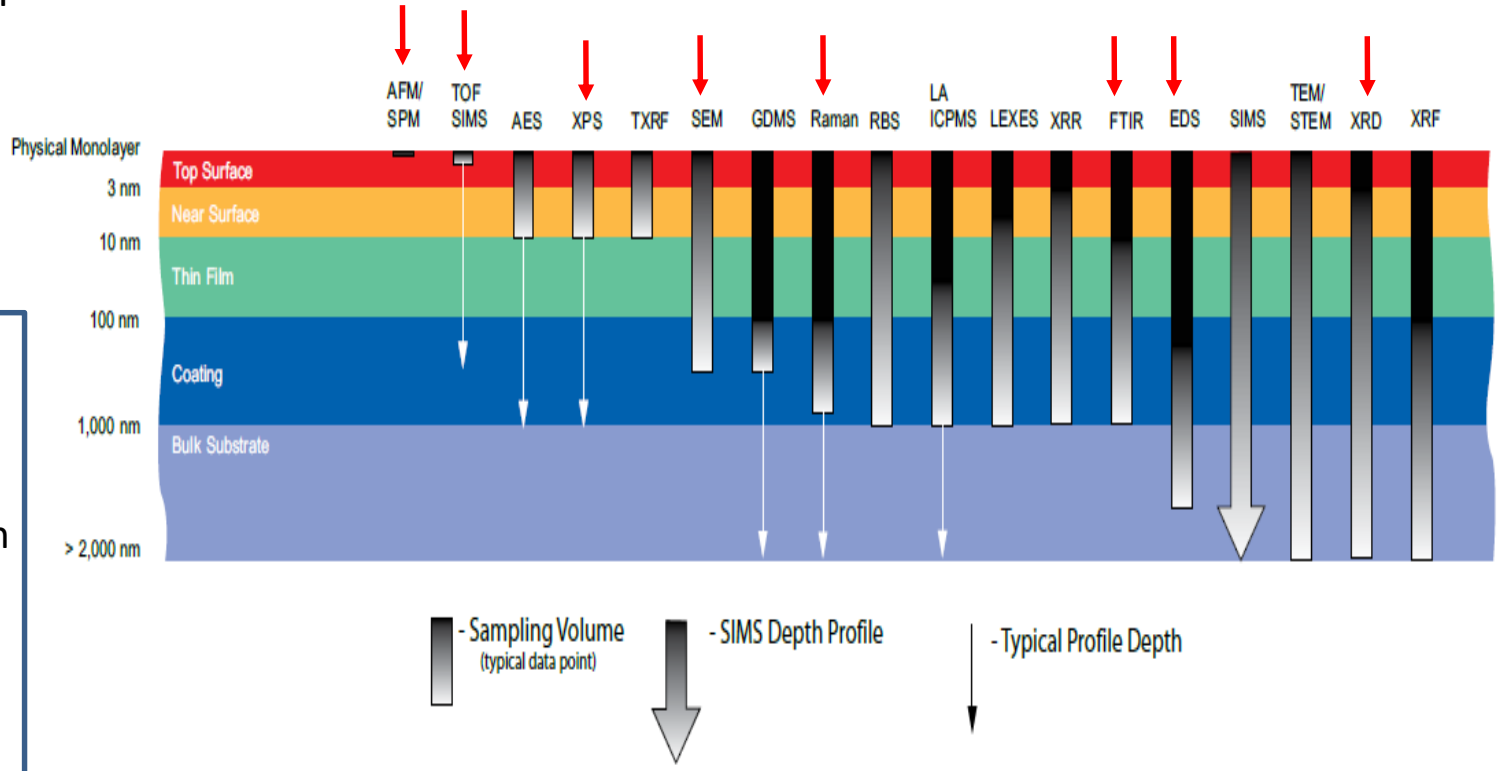
- The goal of this work was to establish unified approach to problems relevant to characterization, through setting analytical protocols adapted to particularity of the analysis, optimizing the existing analytical methods, sampling, handling and measurement protocols as well as interpretation of the results, thus enabling comparison of results between different laboratories.

Physical and chemical techniques in electrode aging studies

- We present a set of complementary analytical techniques which give a detailed characterization of deposits accumulated on MWPC electrodes
- **Multi-layered nature** of deposit demands combination of analytical techniques with **different penetration depths:**

- Atomic Force Microscopy **(AFM)**: No penetration
- Time of Flight Secondary Ion Spectroscopy **(ToF-SIMS)**: 1-2 nm, depth profiling up to several hundred nm
- X-ray Photoelectron spectroscopy **(XPS)**: ~ 5 nm, depth profiling up to 1 µm
- Scanning Electron Microscopy **(SEM/EDXS)**: < 2 µm
- Fourier Transform Infrared **(FTIR)** and Raman Spectroscopy: < 2-3 µm
- X-ray Diffraction **(XRD)**: < 15 µm

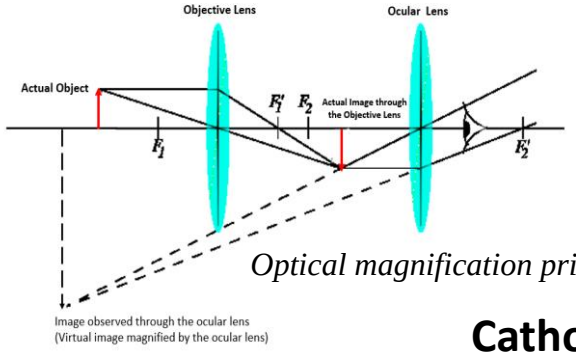
Typical analyses depths of characterization techniques



Cathode investigation techniques	**OM, AFM, SEM, EDS, FTIR, Raman, XRD, XPS, ToF-SIMS**
Anode wire investigation techniques	**OM, SEM, EDS, Raman, XPS, ToF-SIMS (limitations: round shape, small diameter)**

Optical Microscopy (OM)

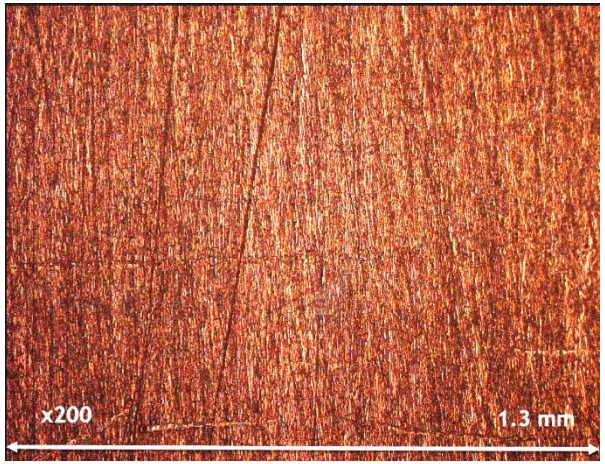
Investigation of large surface areas for cracks, deposits and other defects in reflected light

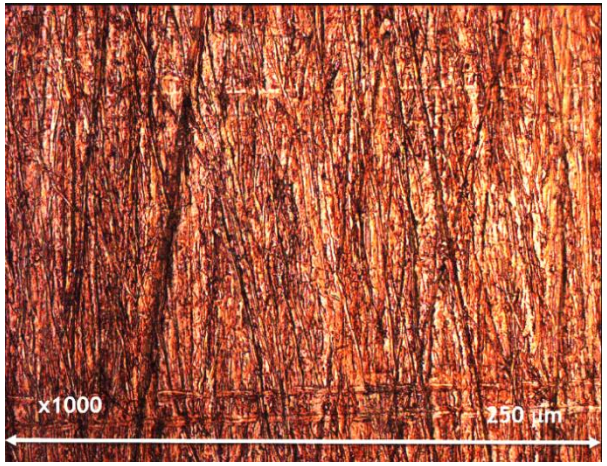


Optical magnification principle

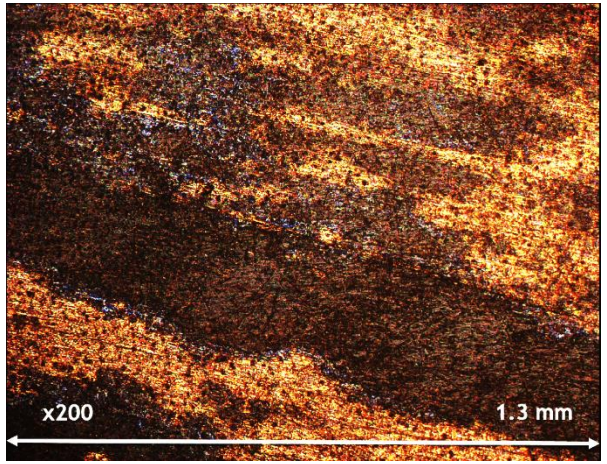
Cathode plates

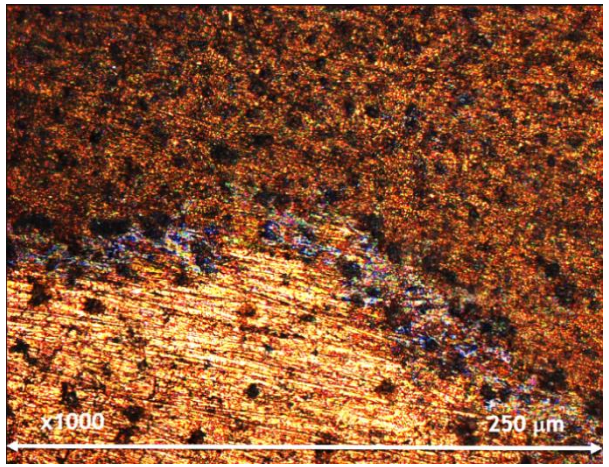
Virgin



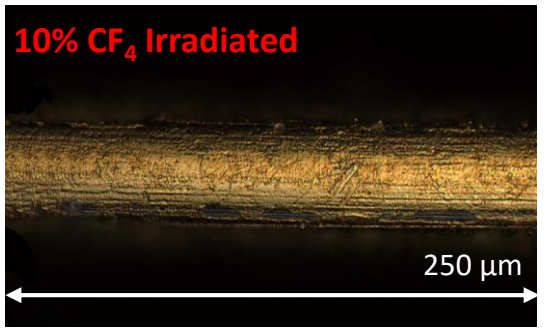


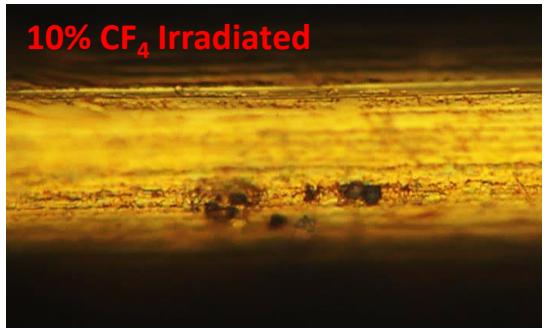
10% CF_4 Irradiated

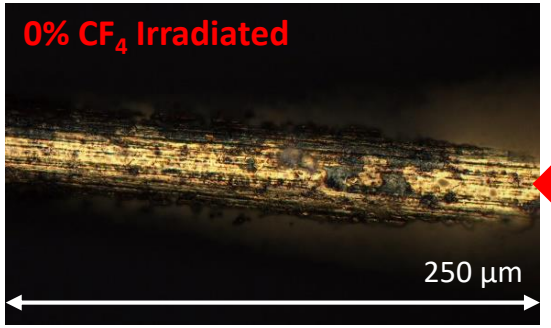


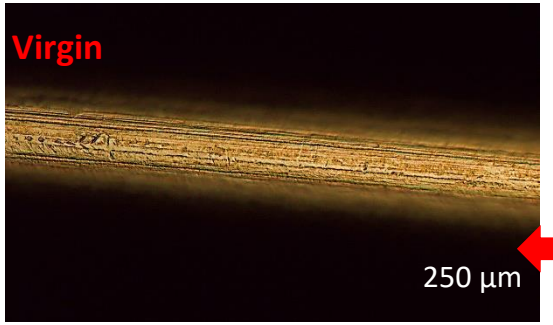


Anode wires





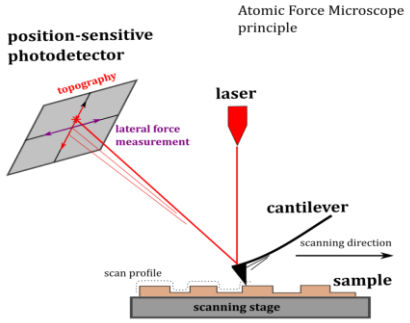




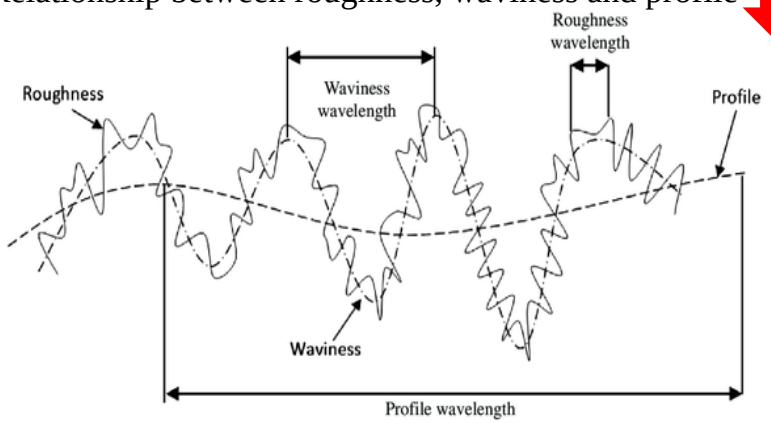
Darkening of the wires

Atomic Force Microscopy (AFM)

Providing a **topographical image** of the surface with atomic resolution



Relationship between roughness, waviness and profile

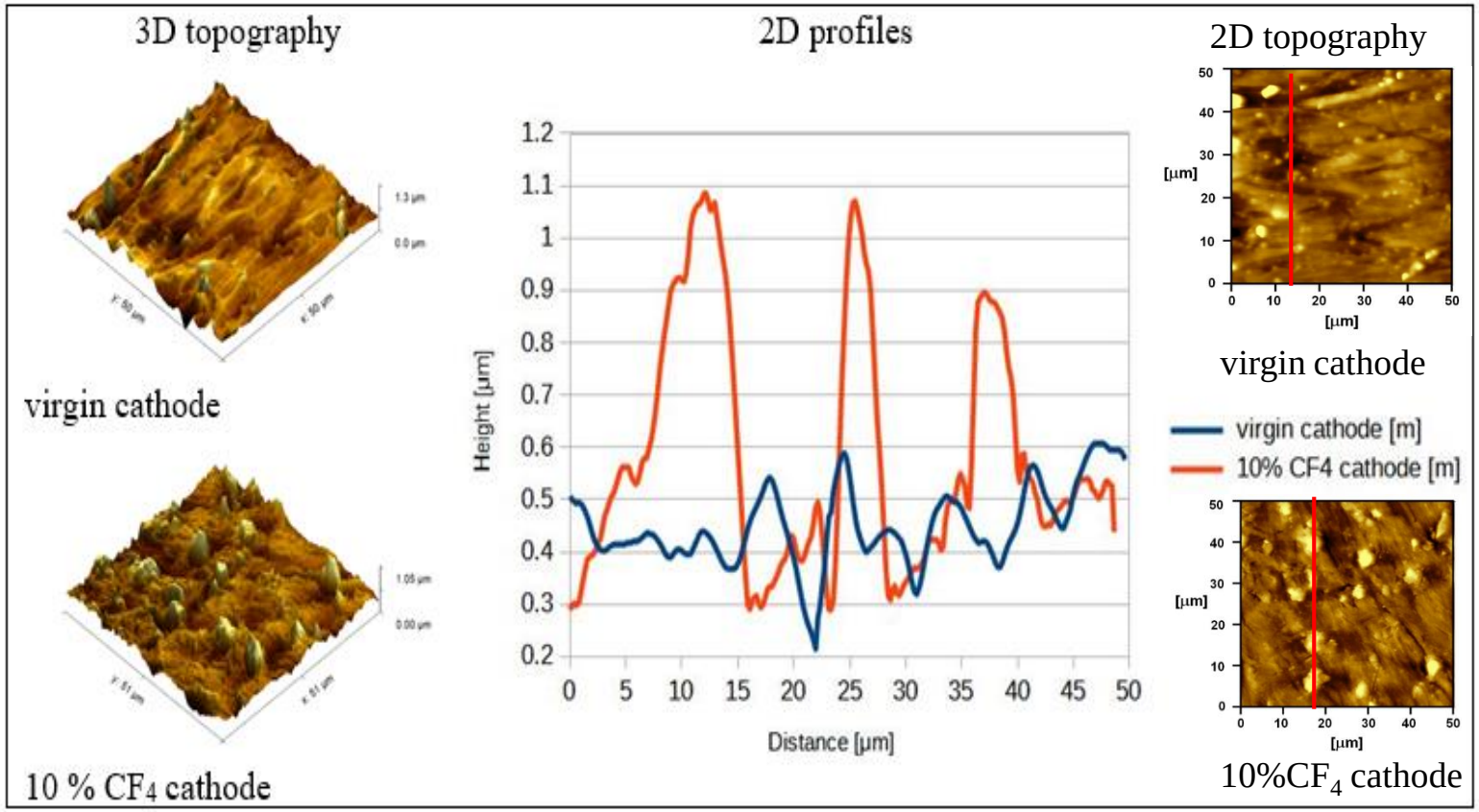


- **Scanning area is chosen (max 100 µm²)**

Ra and **RMS** are both representations of surface roughness, but each is calculated differently.

- Ra is calculated as the **Roughness Average** of a surfaces measured microscopic peaks and valleys.
- RMS is calculated as the **Root Mean Square** of a surfaces measured microscopic peaks and valleys.

Comparison of topography and surface roughness between virgin and aged cathode



Surface roughness parameters (50 µm x 50 µm area)

Sample	Ra (nm)	Rms (nm)
Virgin Cathode	66.5 ± 2.3	89.7 ± 3. 1
Aged Cathode Irr. 10%CF4	84.9 ± 4.9	135.8 ± 6.4

Scanning Electron Microscopy (SEM)

delivers electron image of the surface of examined material in the range of mm to nm thus providing information about the **surface morphology**

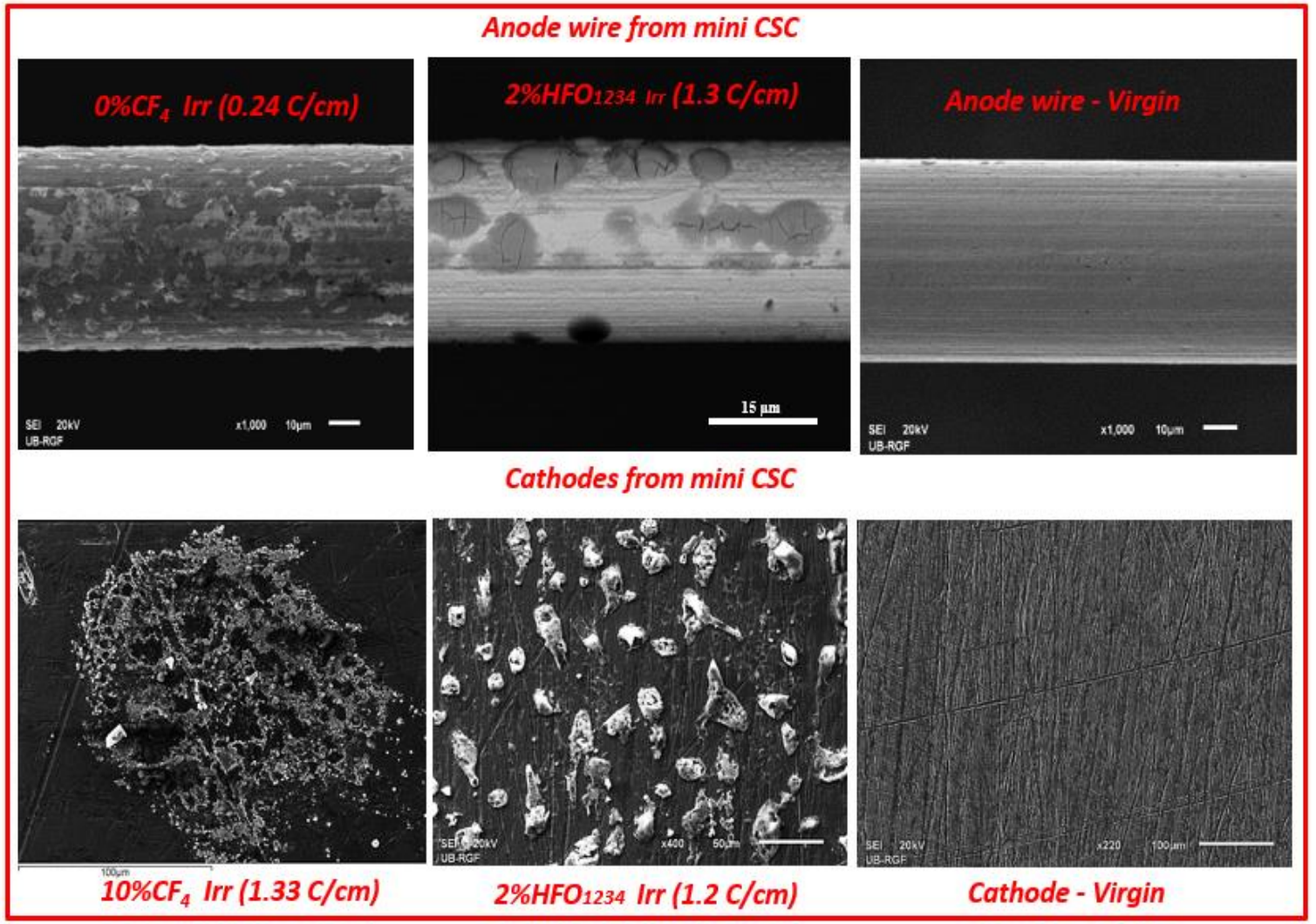
Characteristics

- Method for high resolution surface images
- Uses electrons for imaging
- Measuring in:
  - secondary (SE) and
  - backscattered electron (BSE) contrast
- Magnification range from 100 to 1.000.000
- Non-destructive

- **Surface morphology - Secondary electron (SE) Imaging**

- focused electron beam scanning a sample surface triggers emission of secondary electrons
- Surface-sensitive (topographic) information of the sample
- **Displaying particle morphology (impression of 3D)**

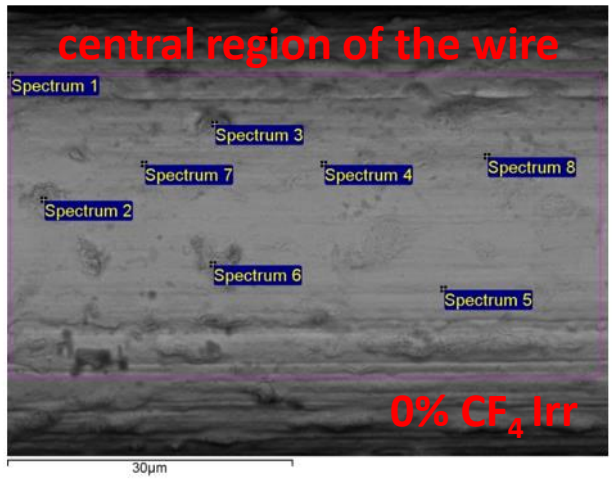
SE micrographs of electrodes from mini CSC

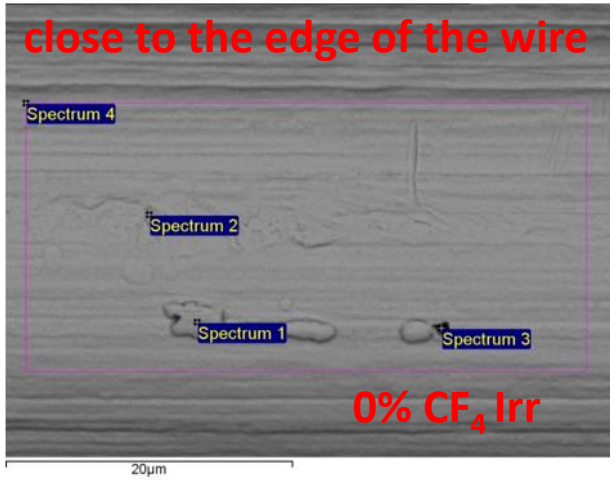


Energy Dispersive X-ray Spectroscopy (EDS)

- Characteristic X-rays produced by the interaction of electrons with the sample are used to **detect and measure the abundance** of elements in the sample **(penetration depth 0.5-2 µm)**

EDS analysis in specific points in two different wire





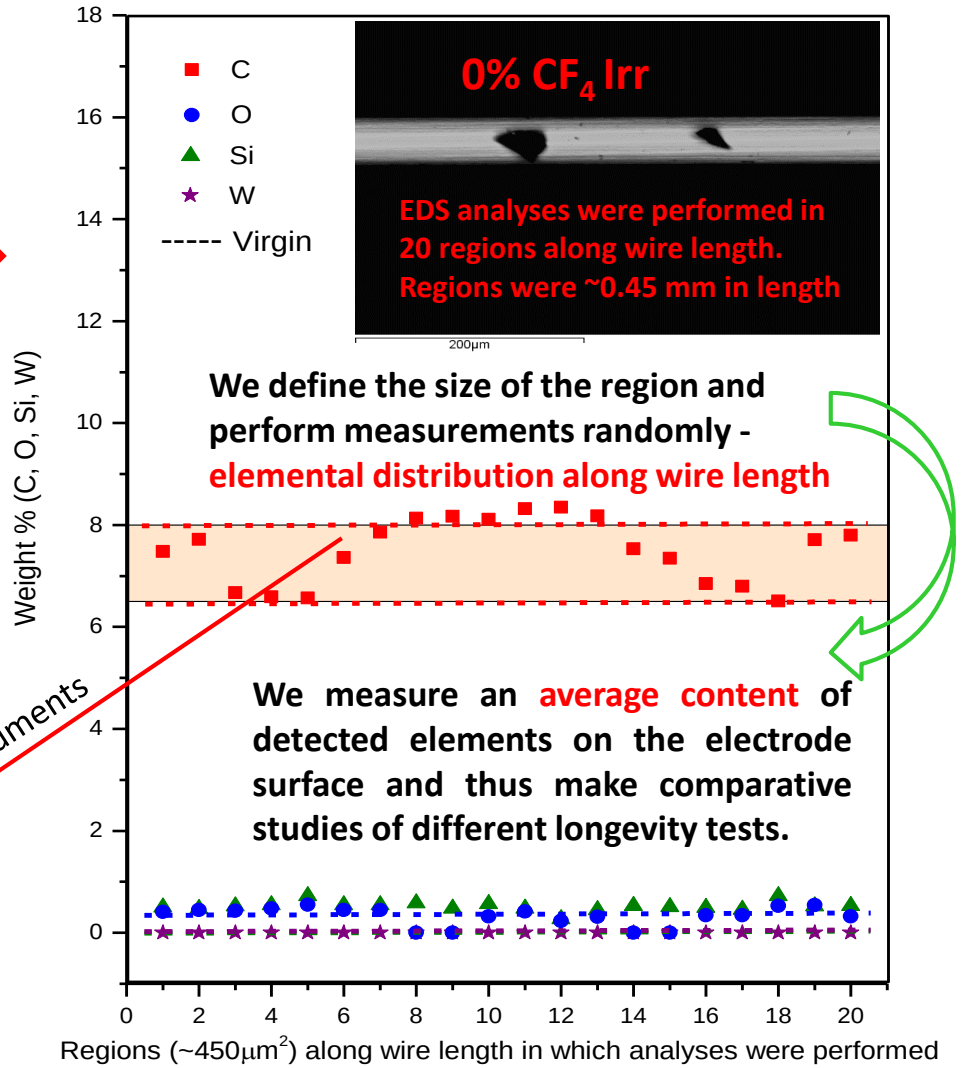
All results in weight%

Spectrum	C	O	F	Si	W	Au
Spectrum 1	8.32	6.84	0.00	1.29	0.00	83.55
Spectrum 2	7.81	5.25	0.78	1.27	0.00	84.89
Spectrum 3	7.09	9.31	0.00	2.07	0.00	81.52
Spectrum 4	9.64	0.00	0.00	0.28	0.00	90.07
Spectrum 5	7.65	0.00	0.00	0.39	0.00	91.96
Spectrum 6	6.76	2.81	0.00	0.90	0.00	89.53
Spectrum 7	5.78	6.84	0.00	1.37	0.00	86.01
Spectrum 8	4.91	7.41	0.00	1.41	0.00	86.27

All results in weight%

Spectrum	C	O	F	Si	W	Au
Spectrum 1	6.63	6.74	0.02	0.00	0.00	86.61
Spectrum 2	5.66	7.81	0.06	1.83	2.96	81.68
Spectrum 3	2.76	8.23	0.33	3.78	17.14	67.76
Spectrum 4	6.09	5.38	0.13	0.00	0.00	88.40

EDS analysis in regions
elemental distribution along wire length



Band of uncertainty for C measured on two different EDS instruments

Risks and limitations

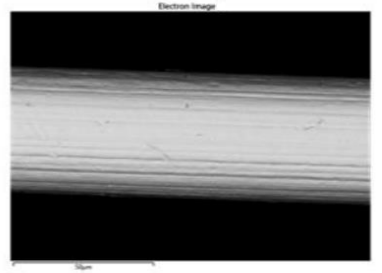
- Detection limit (not suitable for low concentration < 0.1%)
- Not reliable for light elements (semi-quantitative Z<11)
- Volatile-bearing compounds
- Chamber/sample contamination: improper sample handling, reactive samples (interactions with O_2, CO_2, SO_2 etc. from air-forming deposits)

➢ Remedy: e.g. storing the samples in vacuum desiccator

Elemental distribution (X-ray Mapping)

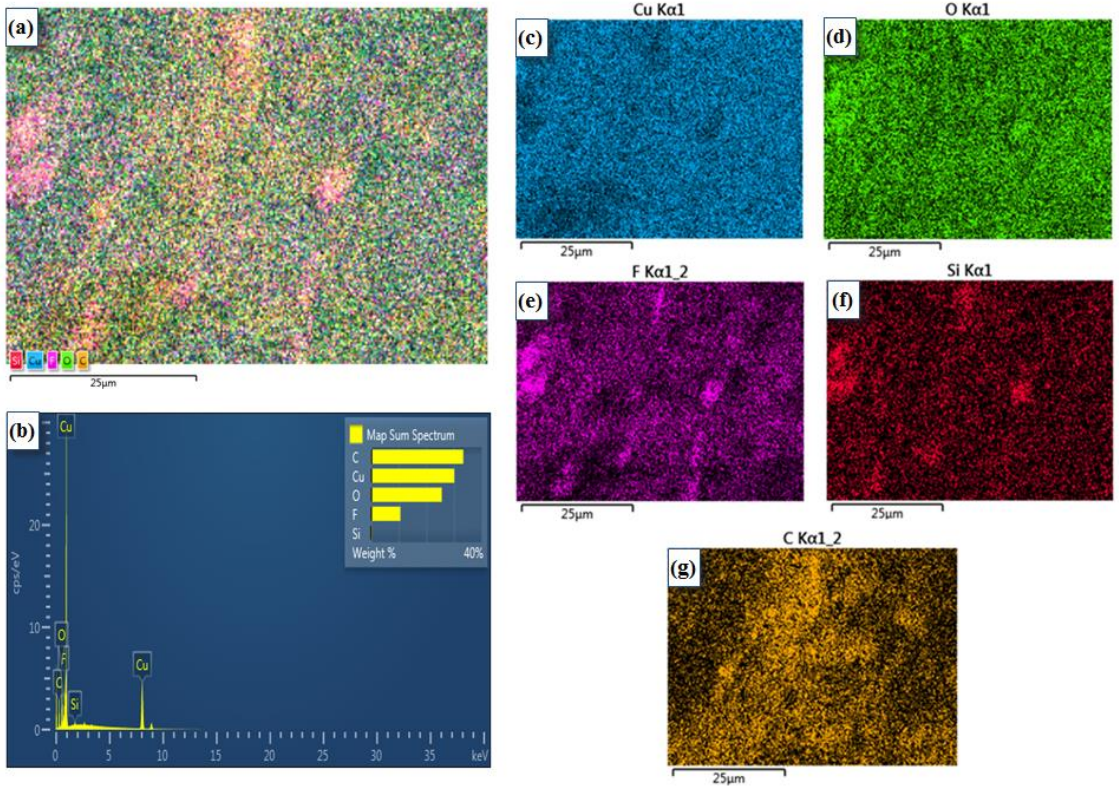
- Characteristic X-rays produced by the interaction of electrons with the sample are used to produce **spatial distribution of individual elements** specified by distinctive colors; brighter areas correspond to a higher concentration of an element of interest.
- The mapping shows a correlation between **morphological features** and the **constituent elements** on the surface and between **concentrations** of the detected elements.

Virgin anode wire



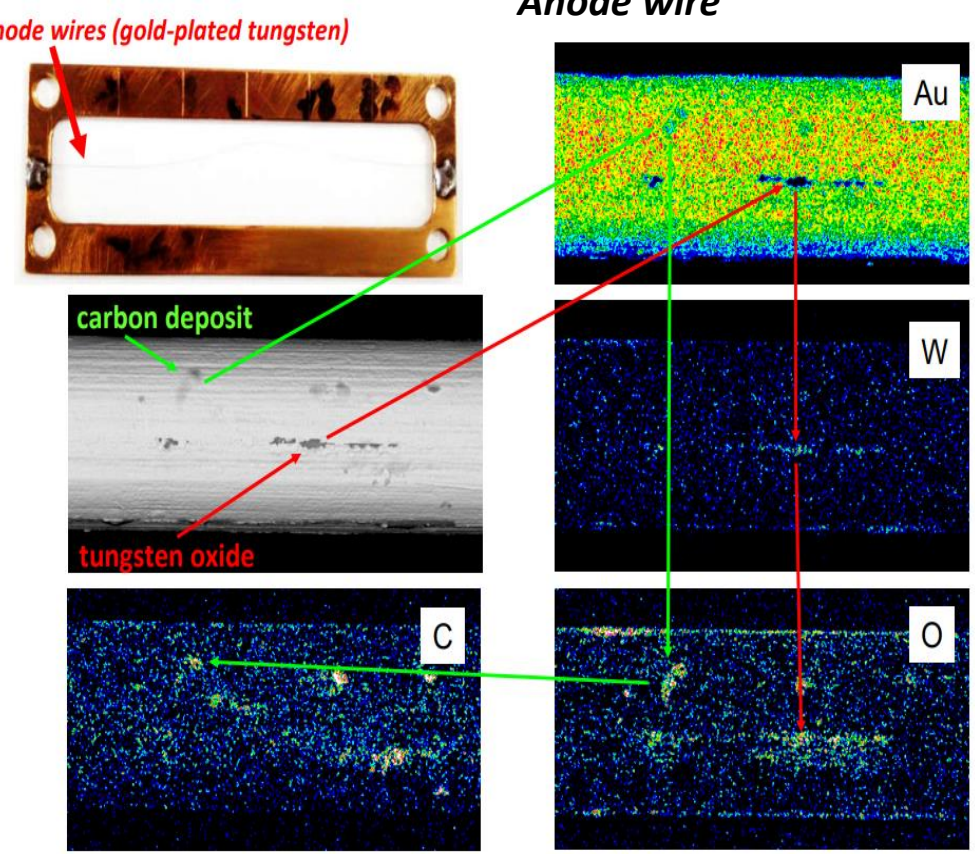
Gas mixture:40%Ar + 50%CO_2+ 10%CF_4

Cathode plate

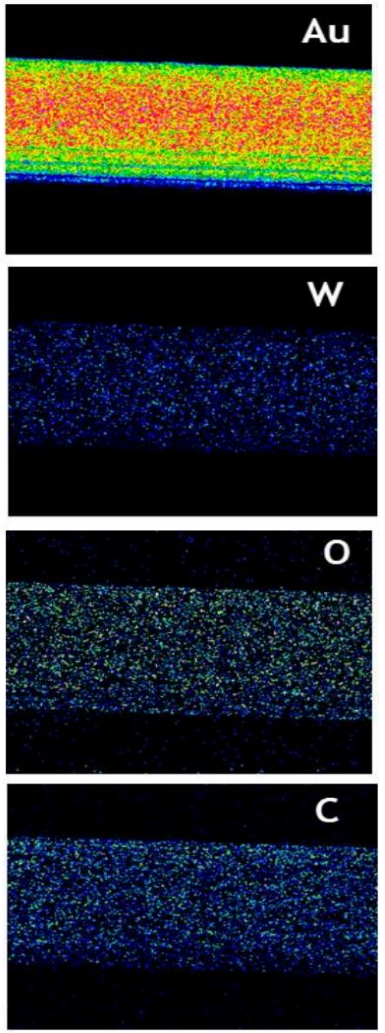


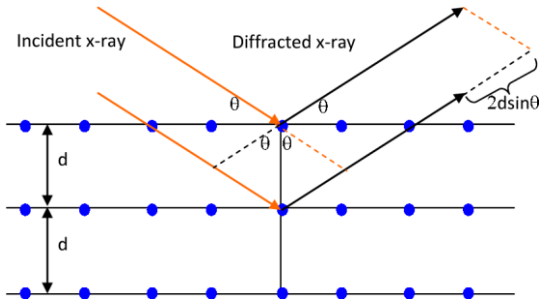
O, F and Si are characterized with matching distribution indicating formation of Si-O-F polymers

Anode wire

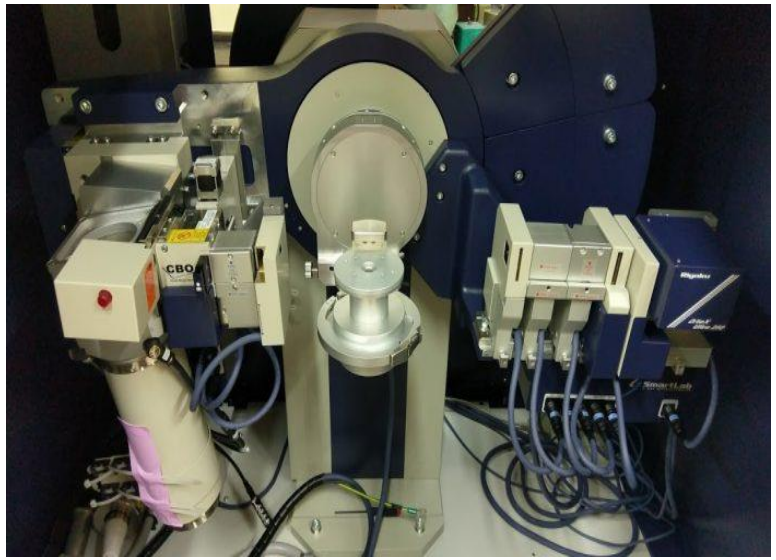


Detection of cracks in gold plating and carbon spots





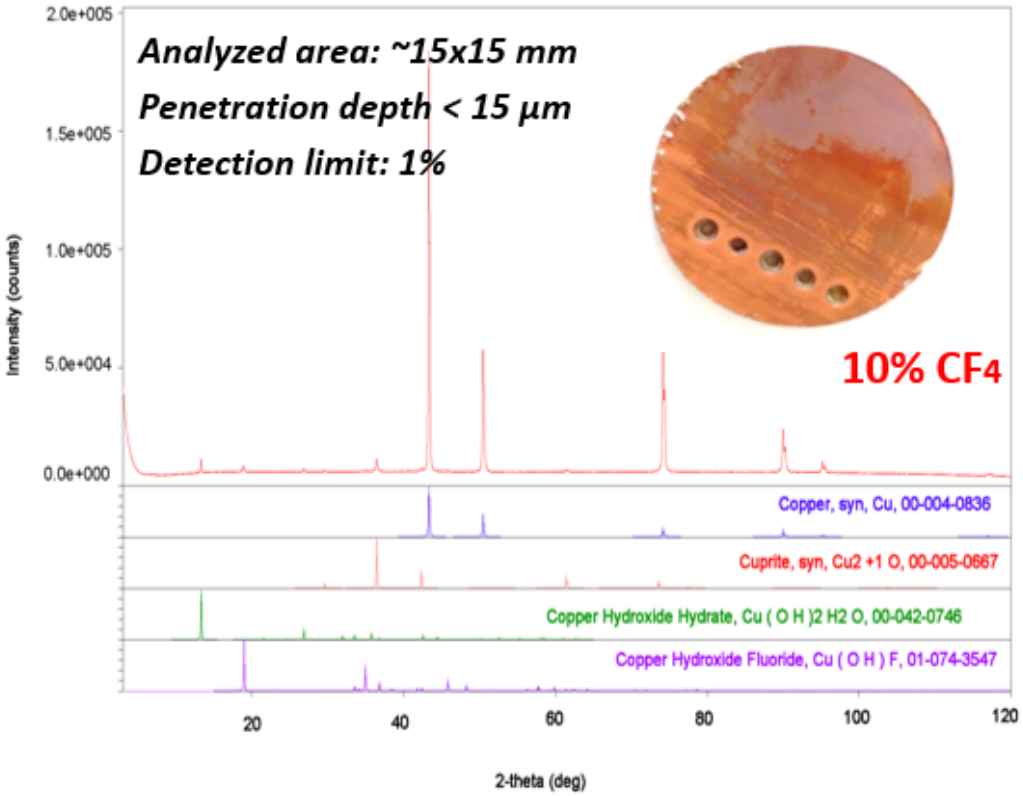
X-Ray Diffraction (XRD)



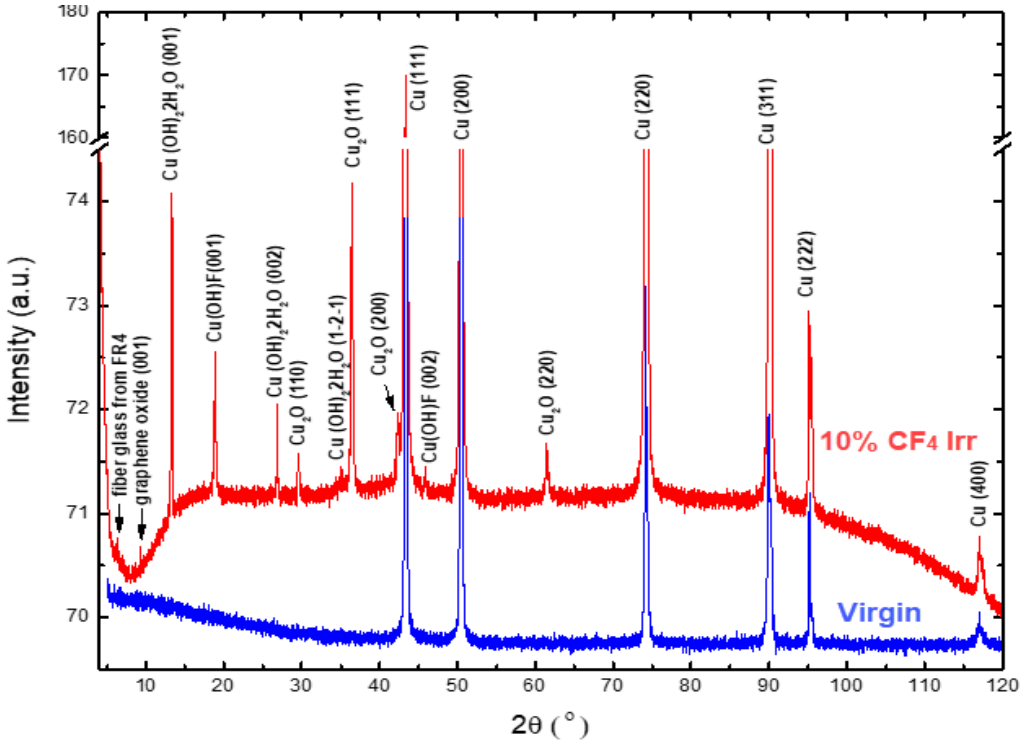
Long range order in crystal structures:

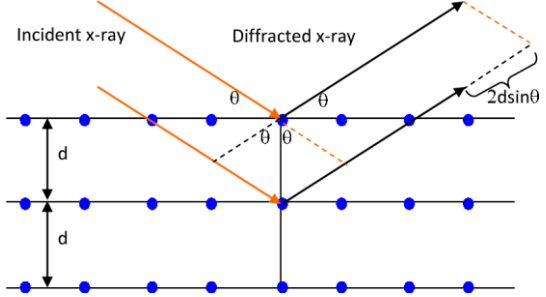
- measures the angle of the beam scattered from crystal planes thus giving the information on periodic atomic arrangements in a given material, which is used for **identification of crystal phases** in material.

Crystal phase identification



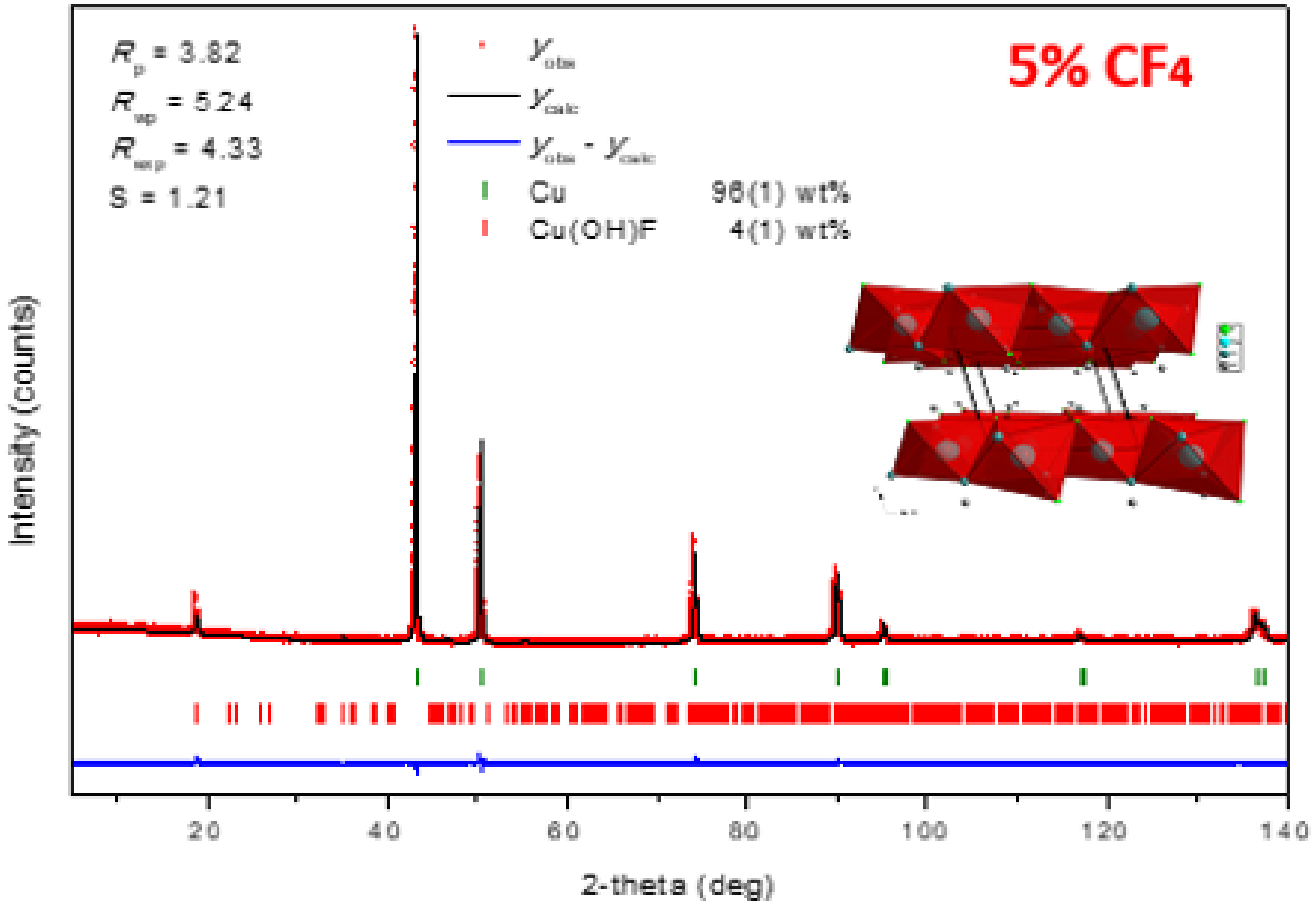
Comparison of XRD patterns of virgin and aged 10% CF_4 cathode





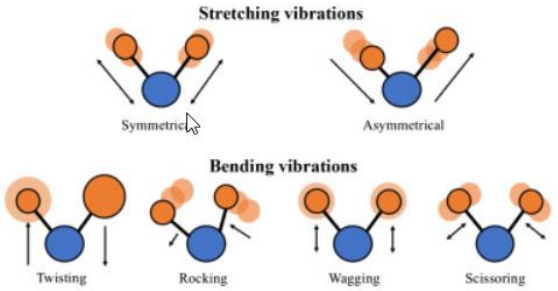
X-Ray Diffraction (XRD)

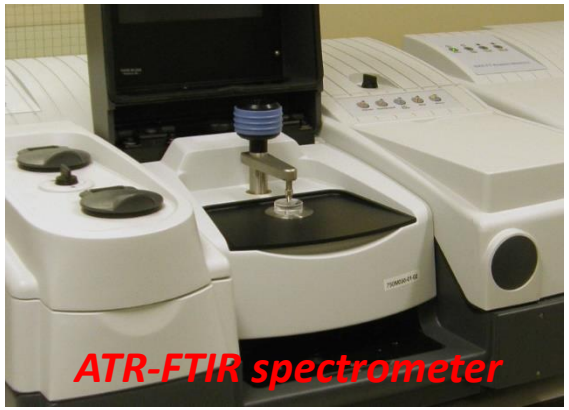
Rietveld refinement
Crystal structure and quantitative analysis of deposit constituents on cathode surface



- Copper hydroxide fluoride Cu(OH)F forms layers of edge-sharing $Cu(OH)_3F_3$ polyhedra, which are connected by hydrogen bonds.
- Quantitative phase analysis showed that **4(1) wt%** of Cu(OH)F and **96(1) wt%** of Cu constitute surface in the center of the irradiated area of cathode in 5 % CF_4 trial.
- Characterization of anode wire by XRD is problematic due to it`s geometry (round shape, small diameter) - upgrade is needed for micro-diffraction measurement – external laboratory).

Vibrational spectroscopy (FTIR and Raman)

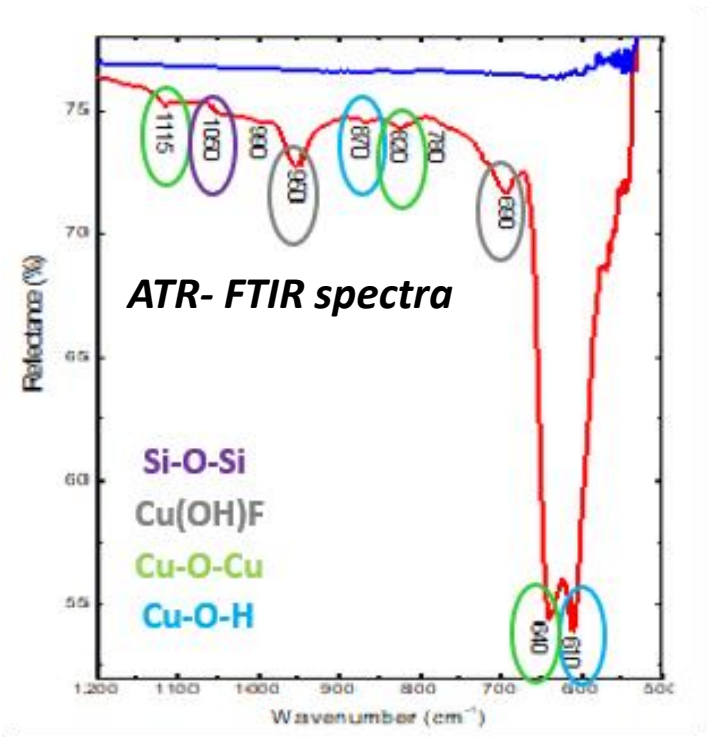


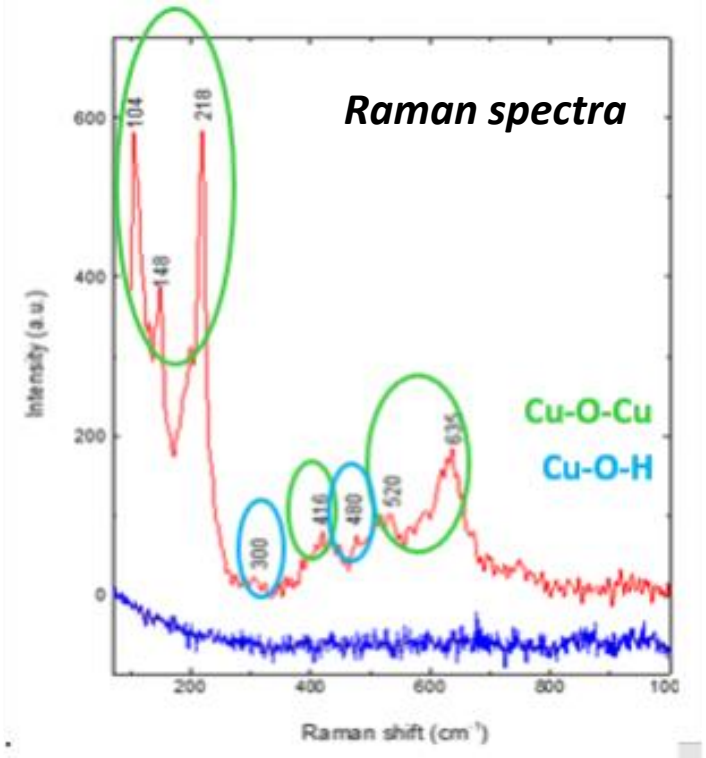


- ***Vibrational (Fourier Transform Infrared – FTIR and Raman) Spectroscopy***

Middle range order in ***crystal*** *and* ***amorphous*** *structures:* measures interaction of radiation with chemical bonds within a material thus giving information on **functional groups within a molecule and energy of chemical bonds**

Comparison of ATR-FTIR and Raman spectra of virgin and aged 10% CF_4 cathode





- Cu-O-Cu, Cu-O-H, Cu-O-F and Si-O-Si bonds are detected on the surface of aged cathode
- Flat line obtained for virgin cathode is due to inactive metal Cu-Cu vibrational modes

➢ **ATR-FTIR spectroscopy**

-penetration depth 0.5 - 2 µm
- detection limit: ~0.1 wt%
- analyzed area ~2x2 mm²

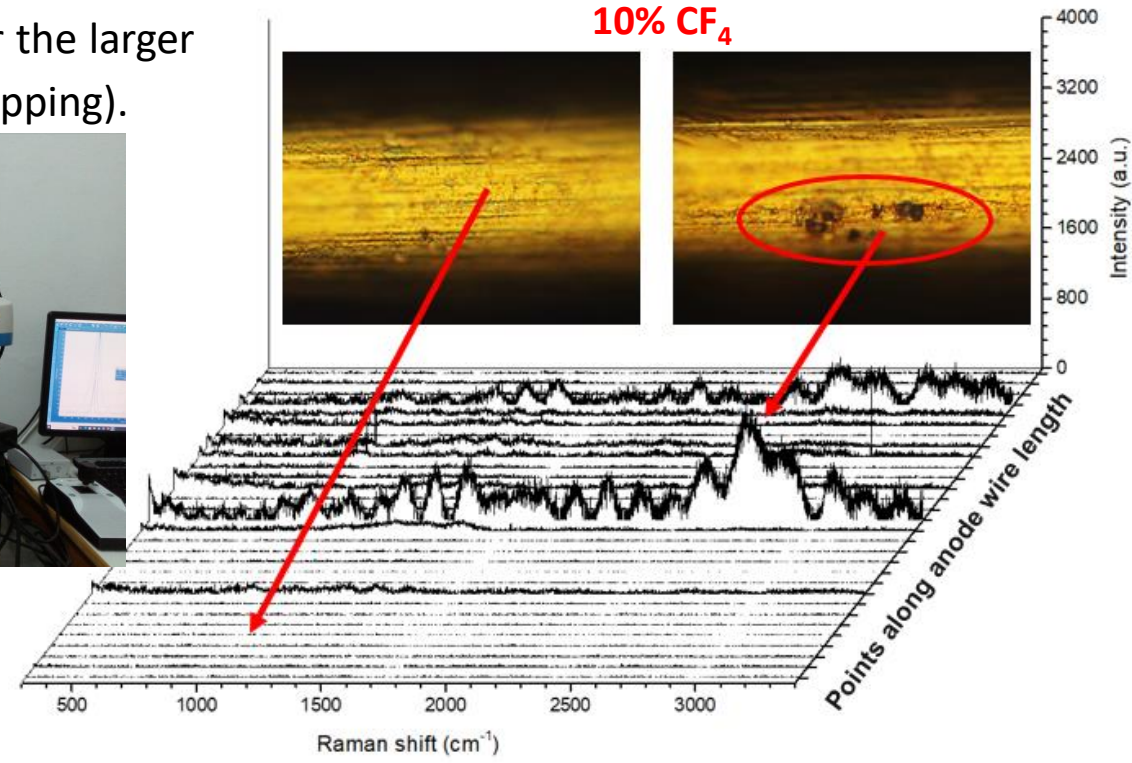
➢ **Raman spectroscopy**

-penetration depth 0.5 - 3 µm
- detection limit: ~0.1 wt%
- analyzed area ~2x2 µm²

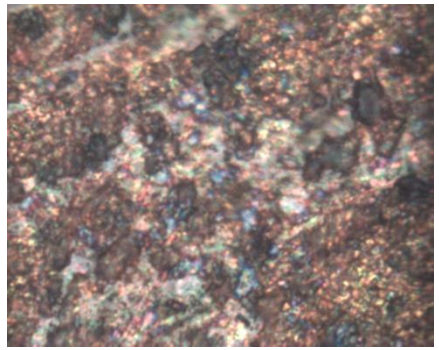
Micro-Raman spectroscopy

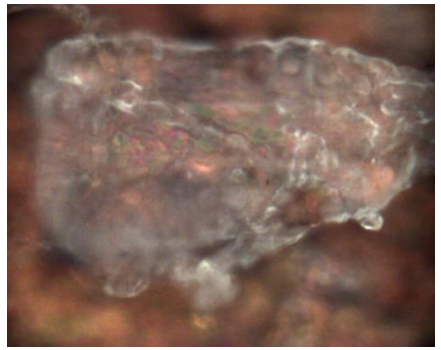
- Coupled with optical microscope, we can **select points of interest (~2µm in diameter)** to investigate structural elements (functional groups) of the deposit constituents formed on electrode surface or perform measurement over the larger area, thus obtaining information on deposit distribution (possibility of mapping).

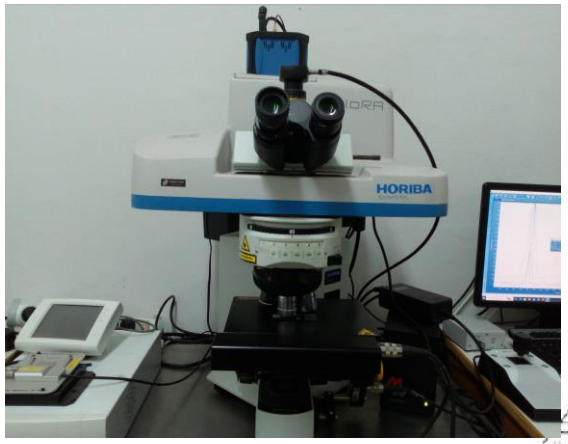
Micro-Raman spectroscopy of anode wires (distribution along wire length)

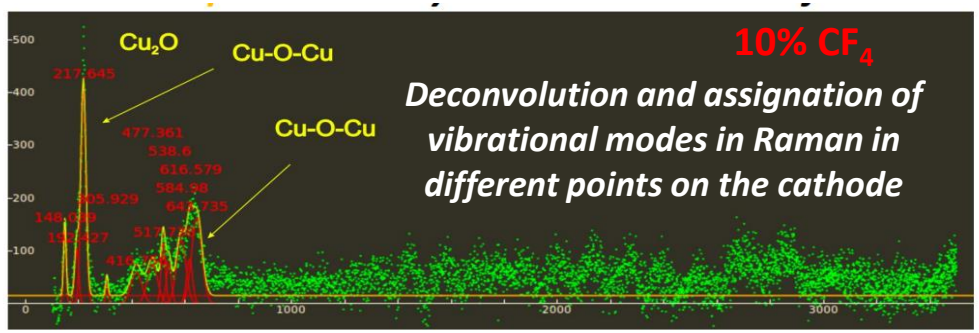


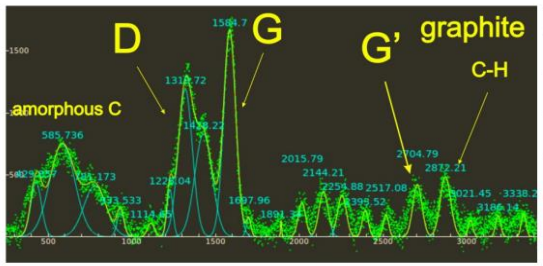
Micro-Raman spectroscopy of cathode surface

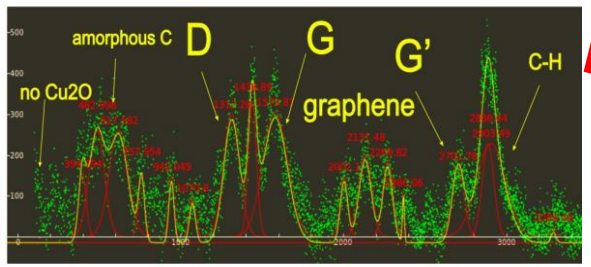












- Raman spectroscopy is the **most valuable technique for characterizing carbon-based structures** as it is sensitive to highly symmetric covalent bonds, which is of particular interest due to different electrical properties of variously doped graphene derivatives.

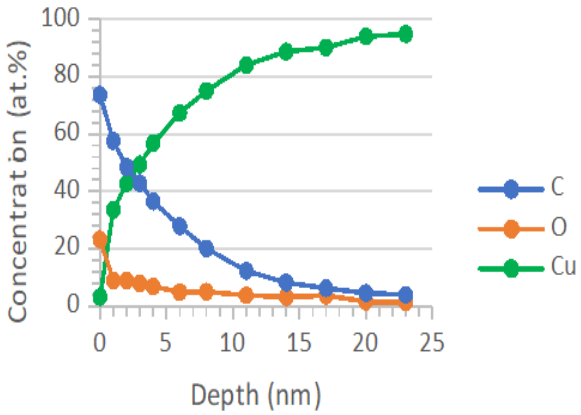
X-ray Photoelectron Spectroscopy (XPS)

- Uses an X-ray beam to excite the elements on the surface of a sample, leading to a release of photoelectrons.
- By analyzing the energy of photoelectrons, the following information are collected: **chemical and electronic state of a sample's elemental components, chemical bonding of elements and quantitative elemental composition**, from surface to a penetration depth of **20-30 nm** in thin films and multilayered structures.

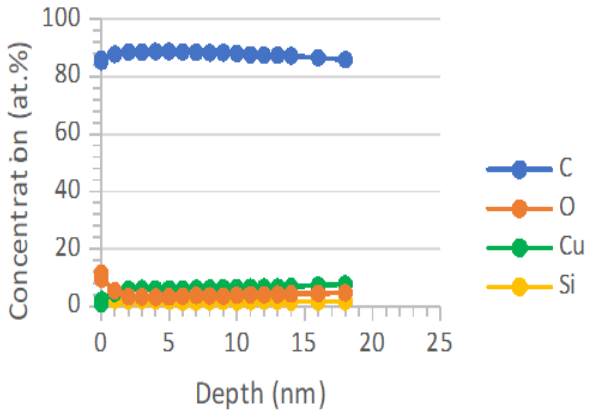
XPS depth profiles

Cathode plates

Virgin

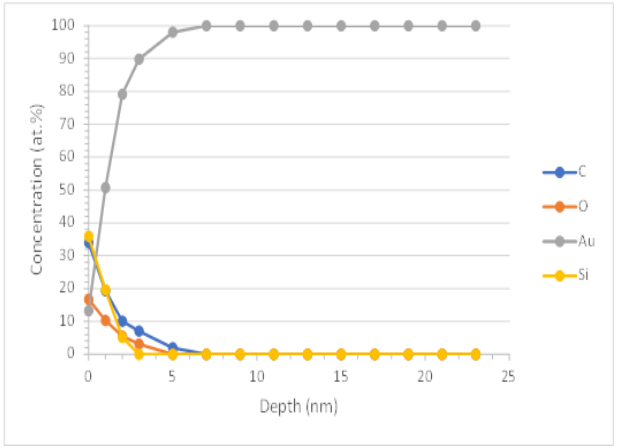


10% CF_4 Irr

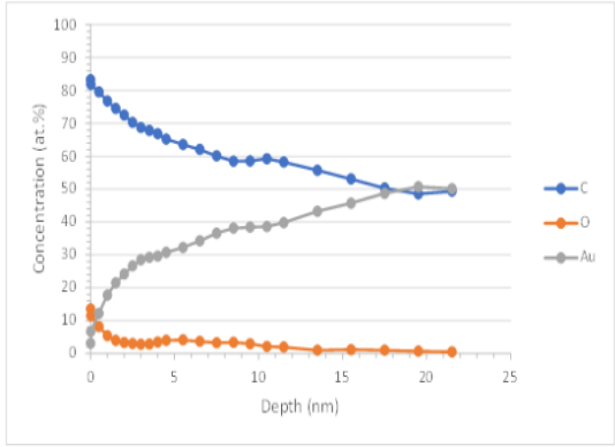


Anode wires

Virgin

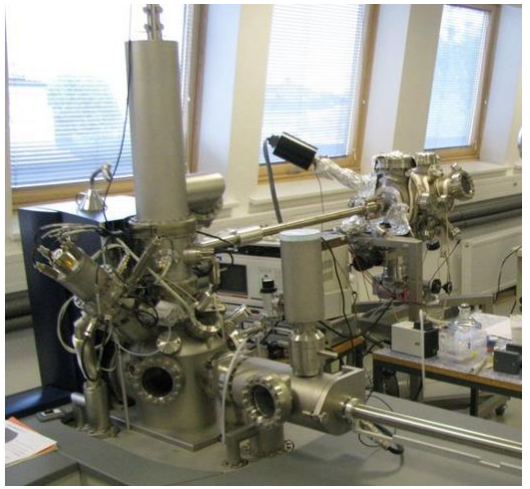


10% CF_4 Irr



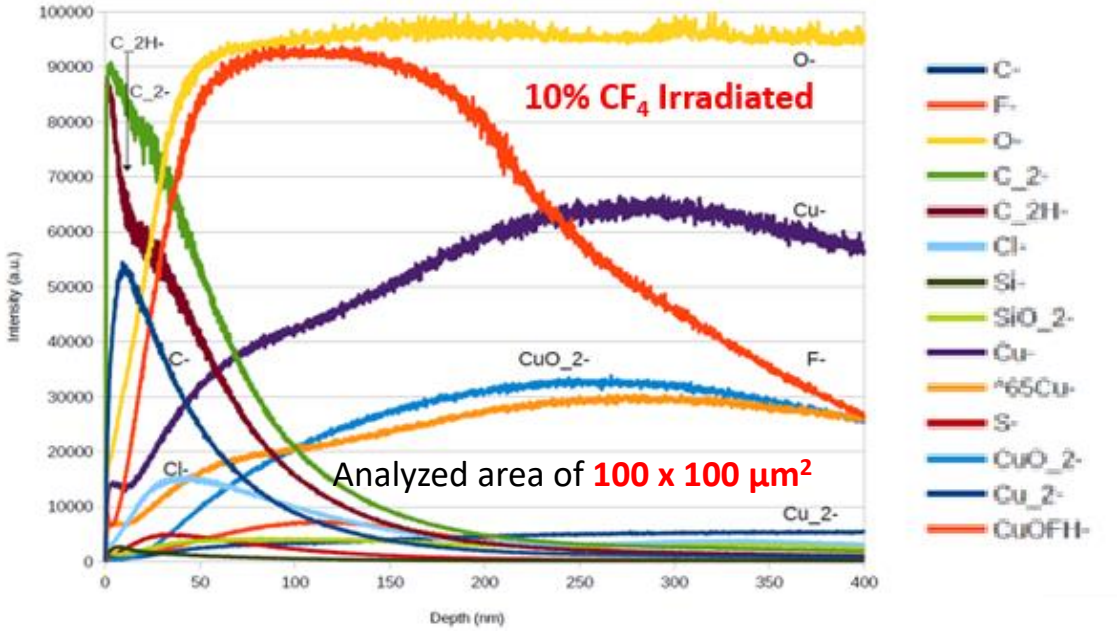
➢ Carbon atomic concentration remained constant **> 80 at%** for aged cathode and up **50 at%** present at aged anode, even at the **20 nm depth**, implying the carbon presence below the surface can be attributed to the carbon deposit, in graphite/graphene form.

Time of Flight - Secondary Ion Mass Spectroscopy (ToF-SIMS)



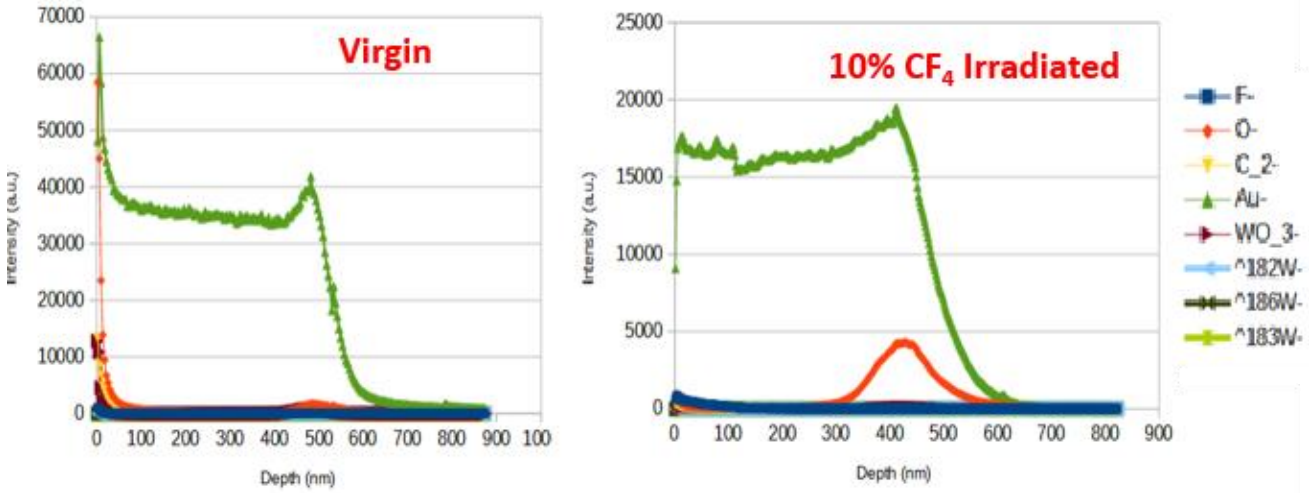
- ToF-SIMS method is used to get additional information about the **depth distribution and the types of species on the surface**. Negative ions emitted from surface are analyzed.
- Quantitative analyses (in %) is not possible with SIMS technique.

Cathode plate



SIMS depth profiles of selected signals obtained on aged cathode versus depth

Anode wires

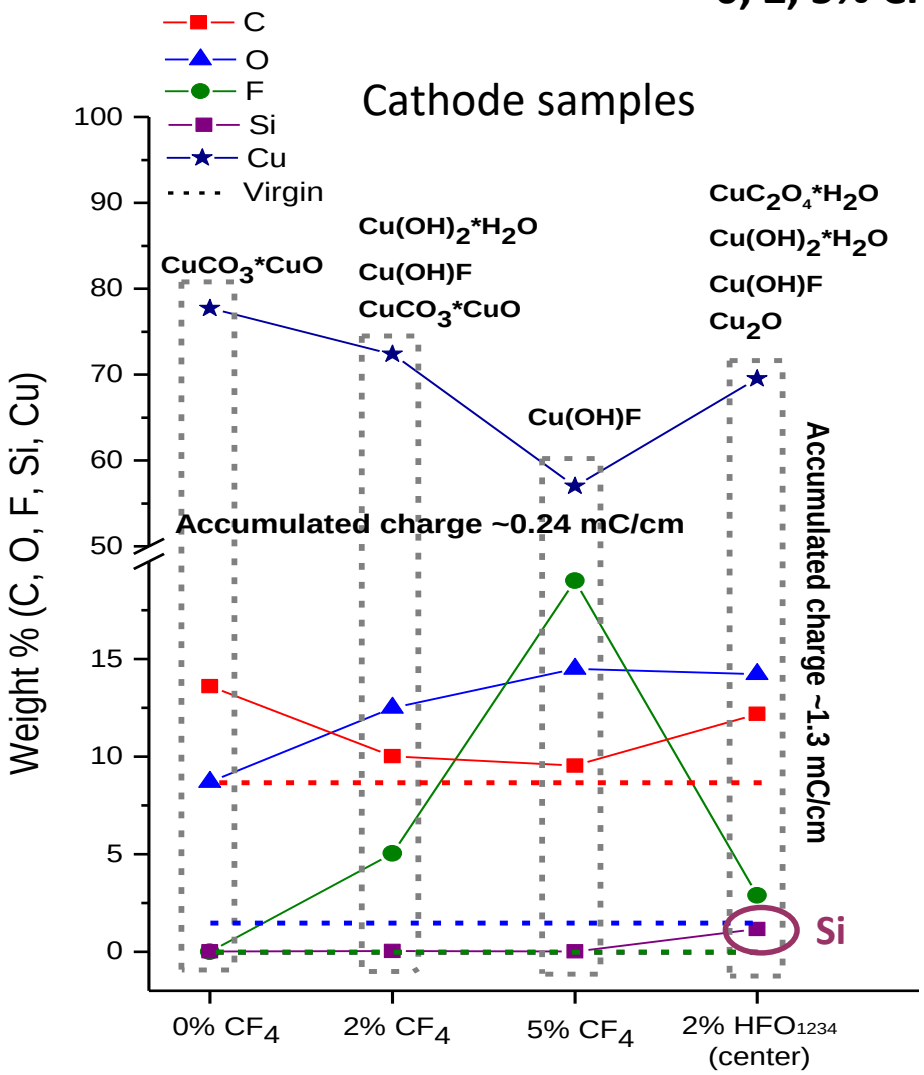


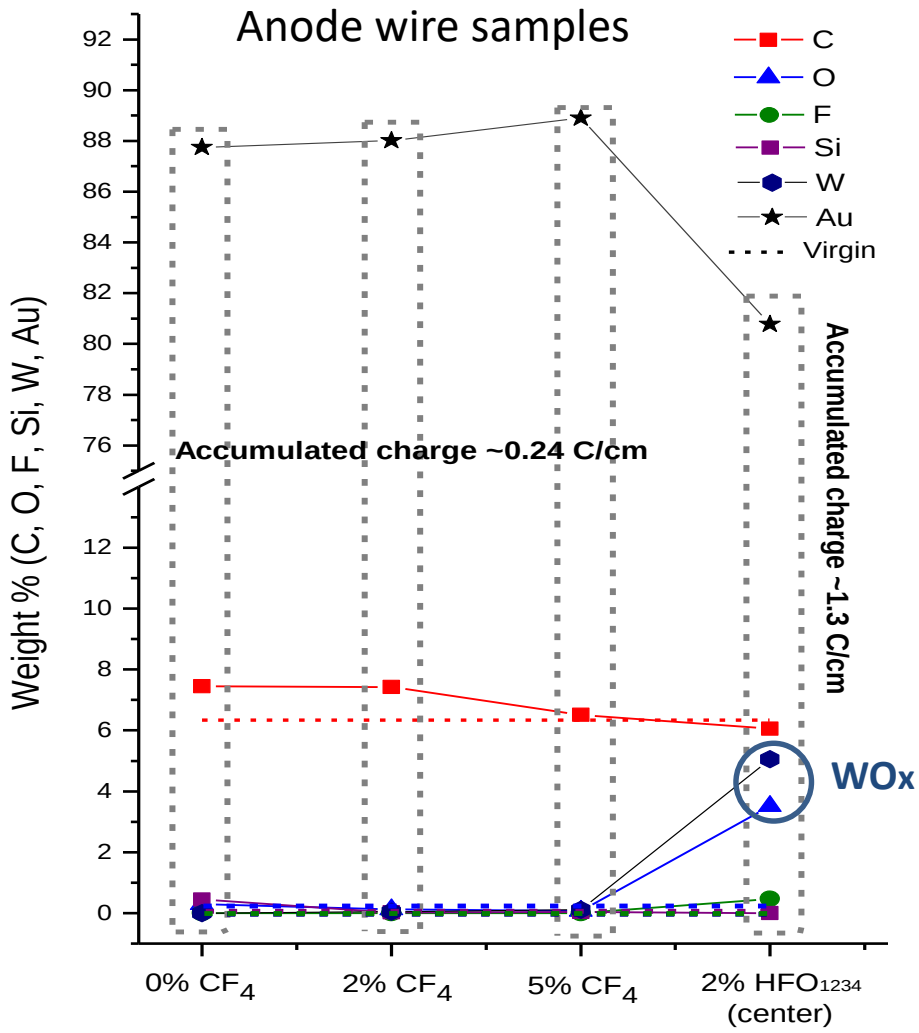
Sputter diagrams of the virgin and aged anode wires
The use of ToF-SIMS for wires is under question

- The cathode surface is covered with Cu-oxide and C-compounds, while Cl, S, C-H can originate from contamination or interaction during operation. Beneath the surface is a region rich with F (300 nm thick), most likely interacting with Cu and Cu-oxide.
- In aged anode increased O signal at Au/W interface is detected.

Summary of obtained results

Comparison of results for irradiated cathode and anode samples
0, 2, 5% CF_4 and 2% HFO1234ze





See the "Studies toward reduction or replacement of CF4 in the CMS CSC working gas mixture" by Katerina Kuznetsova

Conclusion

- Analysis of the microstructure of the deposits by combining various analytical techniques that operate at different scales (nano, micro and meso) with different penetration depth provided detailed analysis of electrode deterioration which can:
  - enable better understanding of the deposition mechanism in plasma chemical reactions
  - further help in evaluating optimal working conditions of proportional gas chambers (selecting optimal gas mixture and construction materials of the detector).

- **The goal** of this work is to establish unified approach to problems relevant to analysis by:
  - standardization of optimized analytical methods, sampling, handling and measurement protocols
  - interpretation of the results

  thus enabling comparison of results between different longevity tests and different laboratories and creating network for exchange of knowledge and ideas.

Future plans

➢ *Eco gas search*

- More studies of CSC with miniCSC using different gases with small prototypes
- Searches for eco gases, ideas what to do with them from the chemistry point of view, prediction of the gas properties (chemical reactivity, electronegativity, ionization properties).
- Optimization of the composition of the working gas mixture to provide similar performance (gas gain) as the currently used.
- Collaboration with CSC
- Open for collaboration with other groups

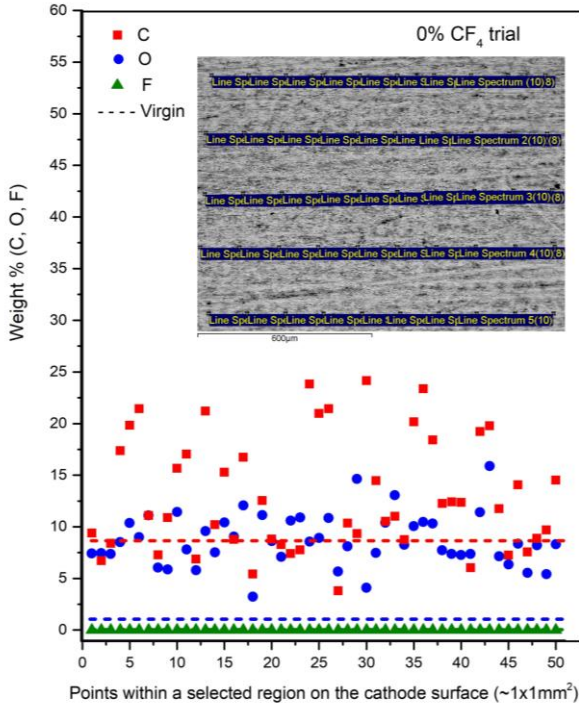
➢ *Adding new analytical techniques and their optimization*

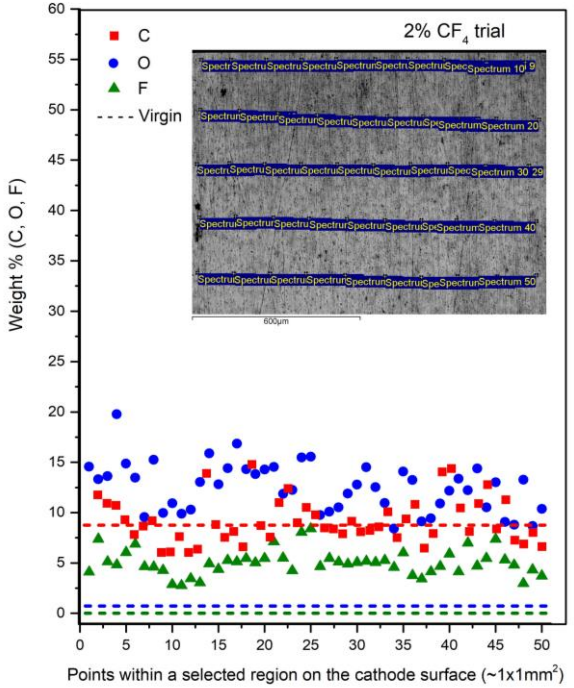
- Introducing additional analytical techniques to have complete set of protocol measurement in order to obtain reliable results.

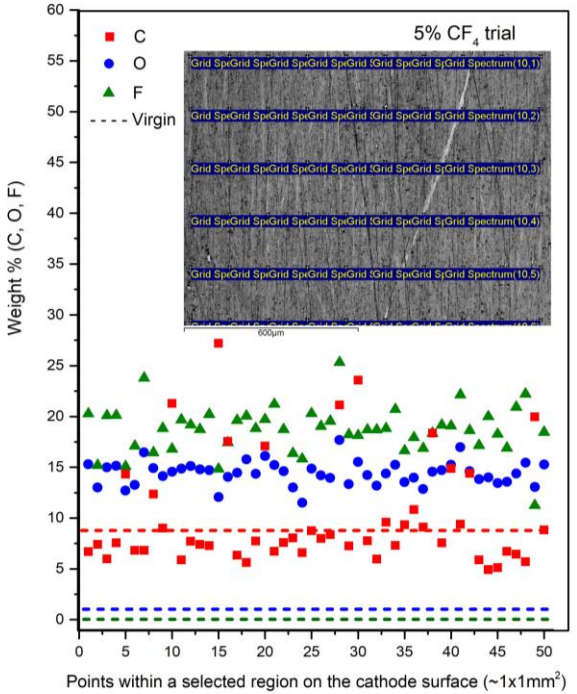
- Overcoming problems by adapting the techniques toward assessing the selected sample properties and establishing methodology for interpretation of acquired results which will be starting point for future research and routine.

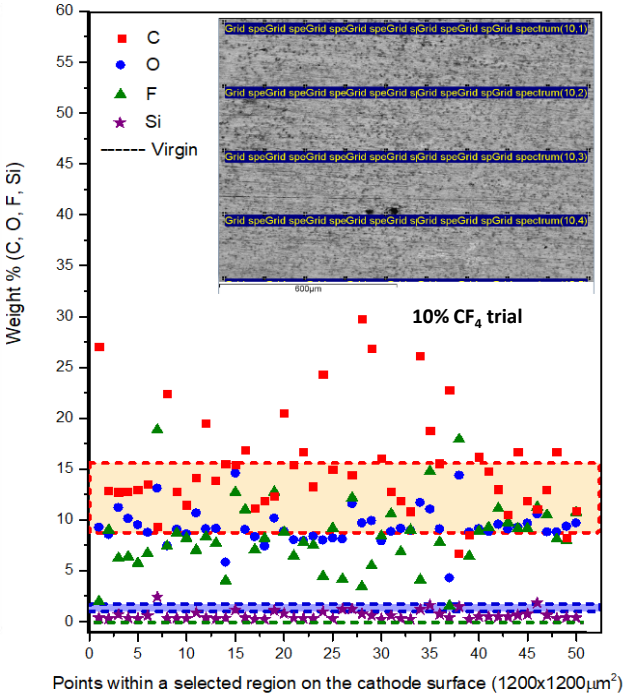
Backup slides

Comparison of elemental distributions over the selected regions of cathodes (0, 2, 5 and 10% CF_4) in the center of irradiated zone



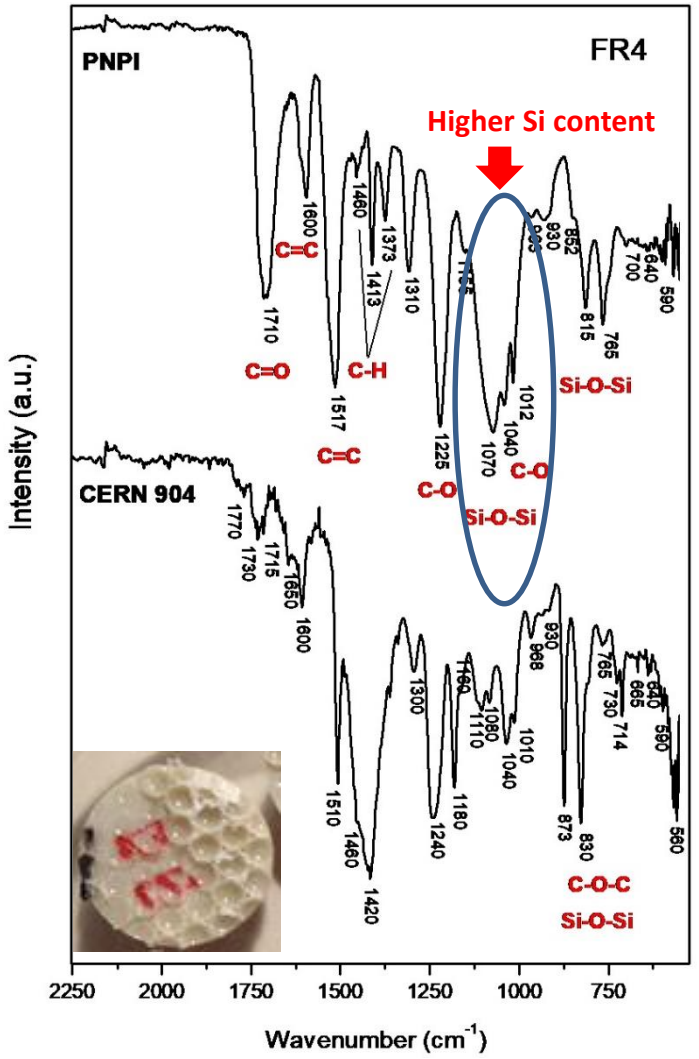






Analysis of FR4 material

Comparison of FTIR spectra of FR4 material from PNPI and CERN 904



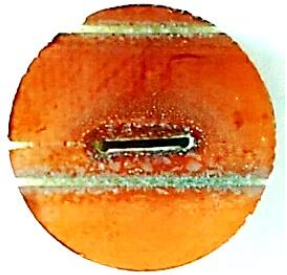
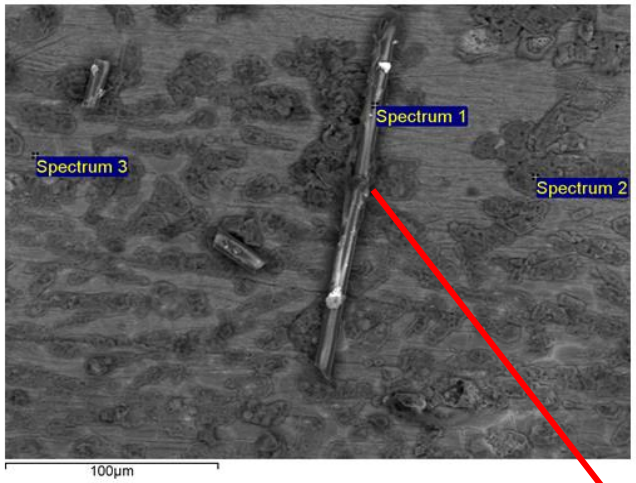
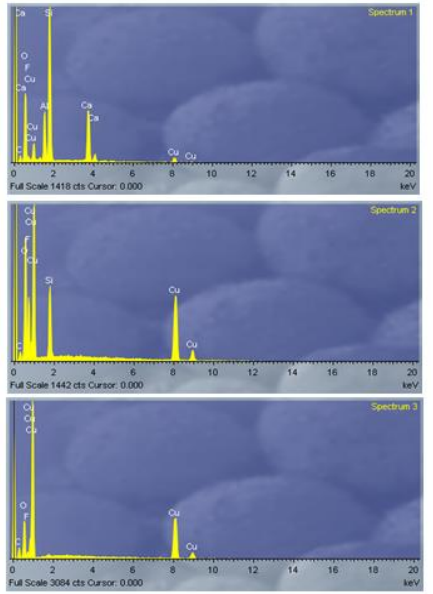


Table 3: Typical constituents of E-Glass [4]

Constituent	Composition (%)
Silicon dioxide (SiO_2)	52-56
Calcium oxide (CaO_2)	16-25
Aluminum oxide (Al_2O_3)	12-16
Boron oxide (B_2O_3)	5-10
Sodium oxide (Na_2O) + Potassium oxide (K_2O)	0-2
Magnesium oxide (MgO)	0-5
Iron oxide (Fe_2O_3)	0.05-0.4
Titanium oxide (TiO_2)	0-0.8
Fluorides	0-1

EDS analysis of the cathode surface (PNPI)





All results in weight%

Spectrum	In stats.	C	O	F	Al	Si	Ca	Cu	Total
Spectrum 1	Yes	9.92	41.72	5.47	5.69	20.95	11.45	4.81	100.00
Spectrum 2	Yes	7.04	23.75	20.75		7.02		41.44	100.00
Spectrum 3	Yes	16.64	20.96	3.59				58.81	100.00

Can samples with different FR4 material be compared?