Physicochemical study of electrode aging in CSC longevity tests using eco-friendly gas mixture $Ar/CO_2/HFO_{1234ze}$

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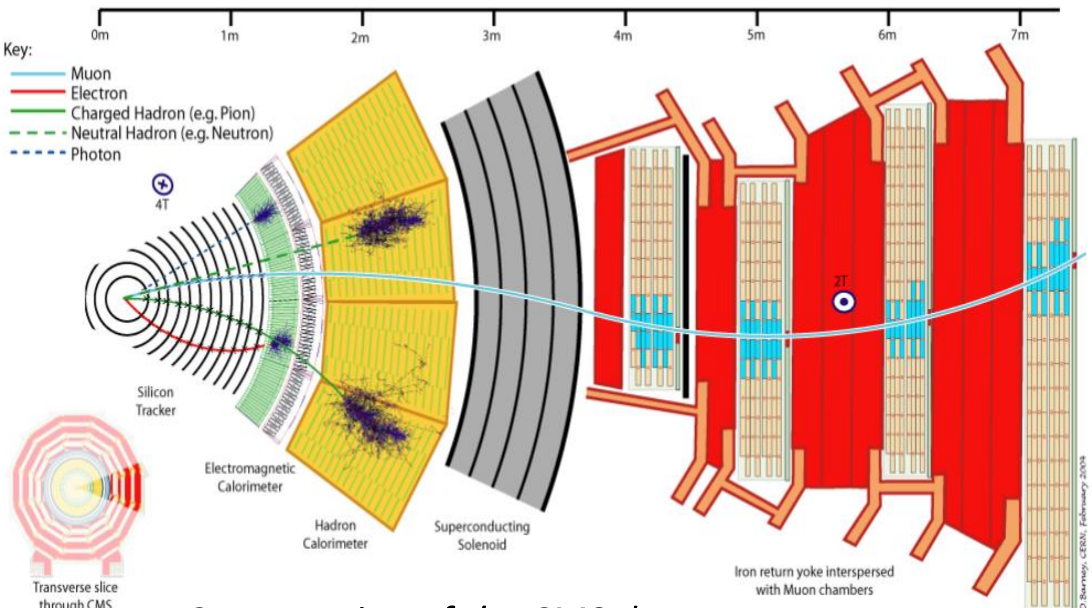
Cathode Strip Chambers (CSCs) in the CMS Muon System

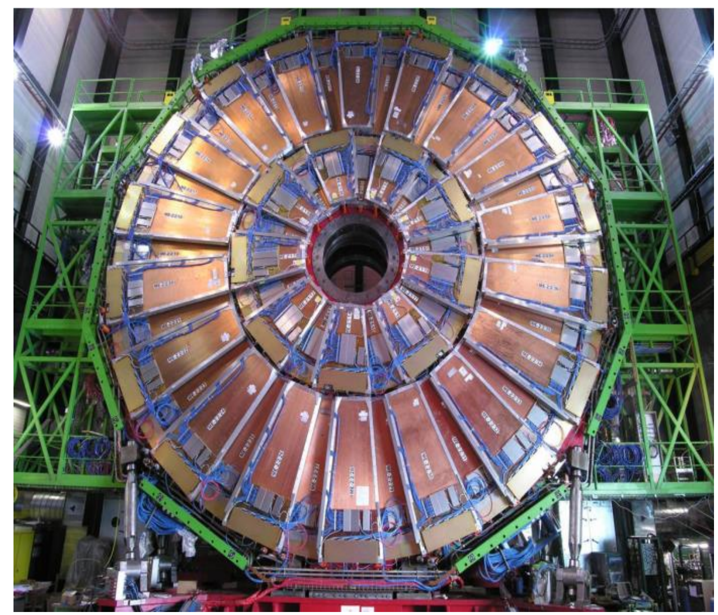
The Compact Muon Solenoid (CMS) experiment at CERN's Large Hadron Collider (LHC) is a general-purpose high-energy proton-proton collider experiment designed to perform both precision measurements of Standard Model phenomena and searches for evidence of Beyond the Standard Model physics.



Cross section of the CMS detector

Objectives of CMS Muon detectors (CSCs, GEMs, DTs, RPCs):

- ➢ muon triggering
- ➢ identification
- ➢ momentum measurement



CMS endcap region includes 540 CSCs

Ionization gas muon detectors:

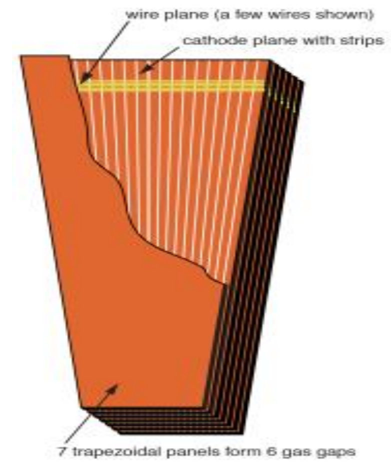
- ➢ **Cathode Strip Chambers (CSCs) - endcap region**
- ➢ Gas Electron Multipliers (GEMs) - endcap region
- ➢ Drift Tubes (DTs) - barrel region
- ➢ Resistive Plate Chambers (RPCs) - both regions

Cathode Strip Chambers (CSCs) in the CMS Muon System

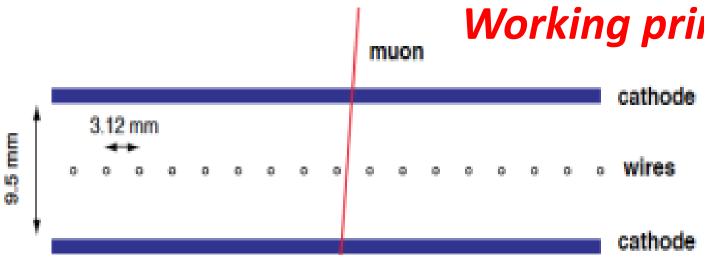
A single CSC chamber is trapezoid-shaped Multi Wire Proportional Chamber (MPWC), composed of alternating layers of cathode strip planes and anode wire planes inside a gas volume.

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

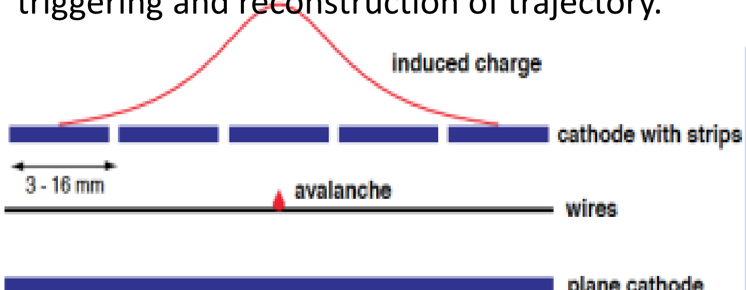
Anode panels: gold-plated tungsten wires, 30 µm in diameter.



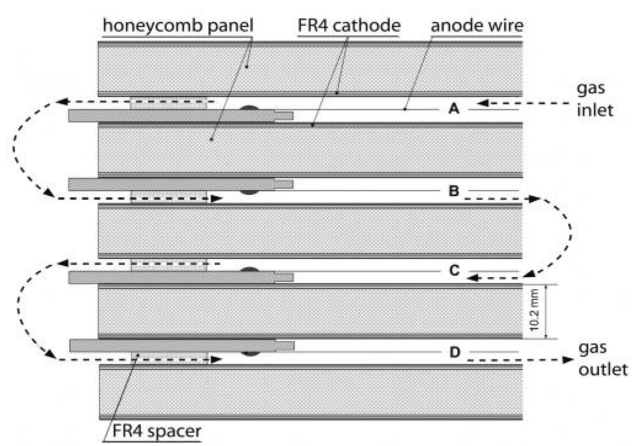
Working principle of CSCs



- Muon causes ionization of gas molecules resulting in an avalanche of electrons around the wire and cathode strips.
- Signals from cathode strips and anode wires are used for triggering and reconstruction of trajectory.



Cross section of a MWPC



- ➢ *High Luminosity operation of the LHC scheduled from 2029 will result in ten times higher integrated luminosity with respect to the initial LHC goal.*
- ➢ *Longevity of the CSC should be provided for 10 years of operation in the High Luminosity conditions.*

Aging Phenomena in Wire Chambers

- **Aging** - synergetic effect of **radiation** and **plasma chemical reactions** that leads to deterioration of electrode surface, causing degradation of operating characteristics of gaseous detectors thus limiting their long-term use in particle physics experiments.

- **Radiation impact:**

formation of blisters, craters, microcracks - leading to erosion of the electrode surface

- **Plasma chemical reaction:**

formation of **conductive** or **insulating** deposit on the electrode surface leading to:
loss of gas gain, occurrence of spontaneous self-sustained discharges (Malter effect)

Observed since development of the first proportional counters (~100 years), aging is still one of the main limitations of gaseous detectors in high rate experiments.

Factors affecting aging

Materials
- Electrode materials
- Sealants
- Adhesives

Gas
- Working gas mixture
- Uncontrolled pollution

- **Optimization of the composition of the working gas mixture and construction materials is of the high importance!**

Choice of Gas Mixture for Use in CSC Wire Chambers

Current Cathode Strip Chamber (CSC) Gas Mixture

40% Ar + 50% CO_2 + 10% CF_4

showed no critical degradation in the chambers work parameters!

Different purpose of each gas:

Ar - chemically inert, ionized by the incoming radiation to produce signals

CO_2 - ”quenching” gas, absorb high-energy photons without re-emission

CF_4 - prevent ”aging” - fluorine radicals liberate carbon and silicon based polymers formed as deposit on the electrode surface

Two Main Motivation to Reduce CF_4

1. **Environmental** - negative impact on atmosphere with GWP of 6630 over 100 years
2. **Economic** – expensive gas

(additional reason: Si-containing material in contact with gas volume is not present in the new CSC design)

Two options:* *reduce *amount of CF_4 or* ***replace*** *CF_4 with a* ***"greener"*** *gas, while preserving the operation and longevity requirement.*
Both options are in the process of testing!

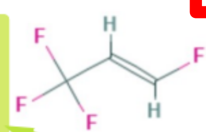
Choice of Gas Mixture for Use in CSC Wire Chambers

Irradiation of CSC prototypes performed at CERN with reduced amount of CF_4 were followed by electrode surface examination done in IGPC and showed carbon contamination of wires for 2 and 0% CF_4.

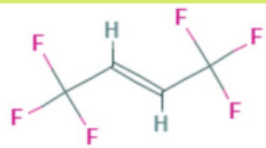
Potential replacement must contain ***F***

At the moment four alternative gases are of interest:

- Hydroflueroolefines (HFC with a double C=C bond) :
  - **HFO-1234ze** (GWP=7) intensively studied for RPC
    - does contain F, but F:C ratio is not optimal **(4:3)**



  - **HFO-1336mzz(E)** (GWP=18)
    - better F:C ratio **(6:4)**
    - but longer molecular chain

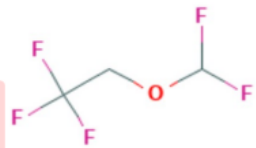


ongoing studies

- Hydro**chloro**fluerocarbons (HCFC) – HCFC-1233zd(E) – under study by ATLAS-RPC ([presented at RPC-2020](#)) - also a replacement of SF6
  - poor F:C ratio (3:3) + chlorine containing
  - probably of low interests for CSC

to be considered

- Hydroflueroethers (HFE, R-O-R') – **HFE-245fa1 (5:3)** and **HFE-143m (3:2)** GWP~700
  - contain oxygen
  - listed in [JINST13 P03012](#) as being of potential interest for gas detectors



Requirements for new gas

- low GWP
- not hazardous
- preventing aging in CSC

taken from K. Kuznetsova "Searches for CF_4 replacement for the CSC gas mixture"

https://indico.cern.ch/event/1022051/contributions/4319536/attachments/2231279/3780771/CSCsearchNewGas_210422_MiniWorkshop.pdf

Choice of Gas Mixture for Use in CSC Wire Chambers

Reasons for choosing HFO1234ze

Allotropic form of tetrafluorpropene $C_3H_2F_4$ ($CF_3CH=CHF$), with the trade name of HFO1234ze

- ✓ zero ozone-depletion potential
- ✓ very low global warming potential
- ✓ not flammable at room temperature
- ✓ low toxicity (considered safe for refrigeration and air-conditioning applications)
- ✓ compatible with most polymeric materials

➢ ***Of high importance***

new mixture has to provide similar performance (gas gain) as the current

- ✓ HFO1234ze is not a strong electronegative gas similarly to CF_4
- ✓ HFO1234ze and CF_4 have similar ionization properties

Unknown parameters of HFO1234ze:

collision cross sections, photon absorption spectrum and the chemical reactivity

Longevity tests with laboratory prototypes of multiwire cathode strip chambers (CSCs) using 40% Ar + 58% CO_2 + 2% HFO1234ze gas mixture

- Longevity studies were performed at the Petersburg Nuclear Physics Institute (PNPI) with laboratory prototypes of multiwire cathode strip chambers (CSCs) of the CMS experiment.

- The goal: to estimate the possibility of using eco-friendly HFO1234ze instead of CF_4 in gaseous mixtures and explore the degradation of the functional characteristics of a prototype CSC detector exposed by intensive irradiation.

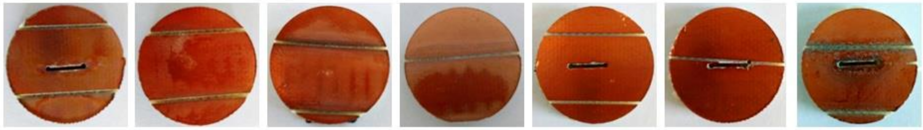
- No gas gain reduction was seen during the tests, though significant increase of the dark current was observed.

- Analysis of deposit formed on the electrode surface was performed at Institute of General and Physical Chemistry (IGPC), Belgrade. Electrodes were provided by colleagues from PNPI (G. Gavrilov).

Cathode and anode samples of mini CSC from PNPI

Gas mixture 40%Ar + 58%CO_2 + 2%HFO1234ze, irradiated up to 1.2 C/cm

Cathode samples: copper-clad FR4 plates



E – center of irradiation zone

EH – intermediate zone ~ 5cm apart from the center

EF – intermediate zone ~ 5cm apart from the center

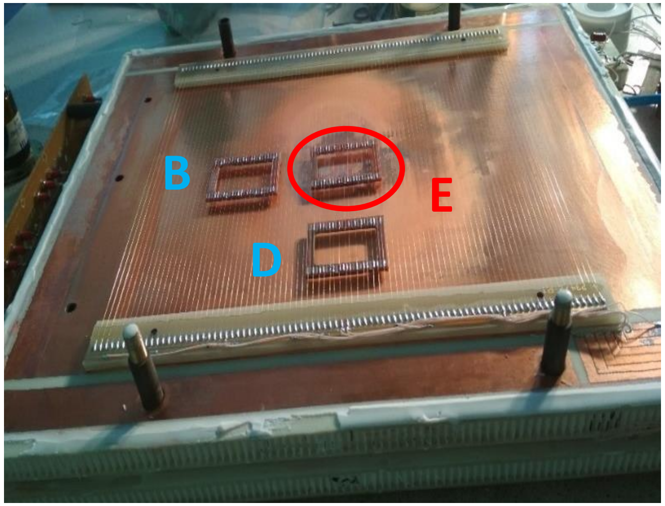
EC – intermediate zone ~ 5cm apart from the center

A – edge (corner) area ~ 10cm apart from the center

C – edge (corner) area ~ 10cm apart from the center

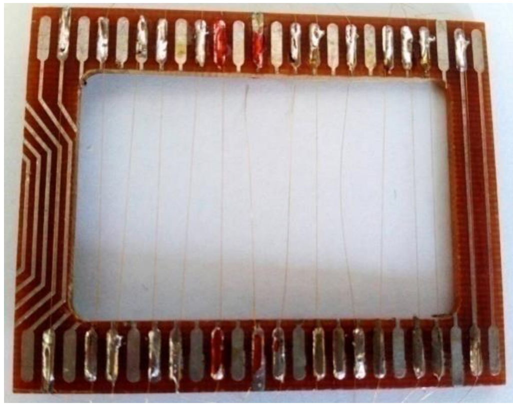
F – edge (middle) area ~ 8cm apart from the center

Anode samples: gold-plated tungsten wires



Central zone E

acc. charge 1.189 C/cm, ionization current 7 uA



Characterization techniques

Deposit was analyzed using non-destructive techniques

- ***Scanning Electron Microscopy (SEM)***

produces 3D images of a sample by scanning the surface with a focused beam of electrons which interact with atoms in the sample, thus giving information about the surface morphology of the material

- ***Energy Dispersive X-ray Spectroscopy (EDS)***

characteristic X-rays produced by the interaction of electrons with the sample are used to map the distribution and estimate the abundance of elements in the sample, i.e., elemental analysis of the material surface (penetration depth 0.5 - 2 µm, detection of elements Z≥5, detection limit: ~ 0.1 wt%)

- ***X-Ray Diffraction Analysis (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 material (analyzed area: ~15x15mm, penetration depth < 15 µm, detection limit: 1%)

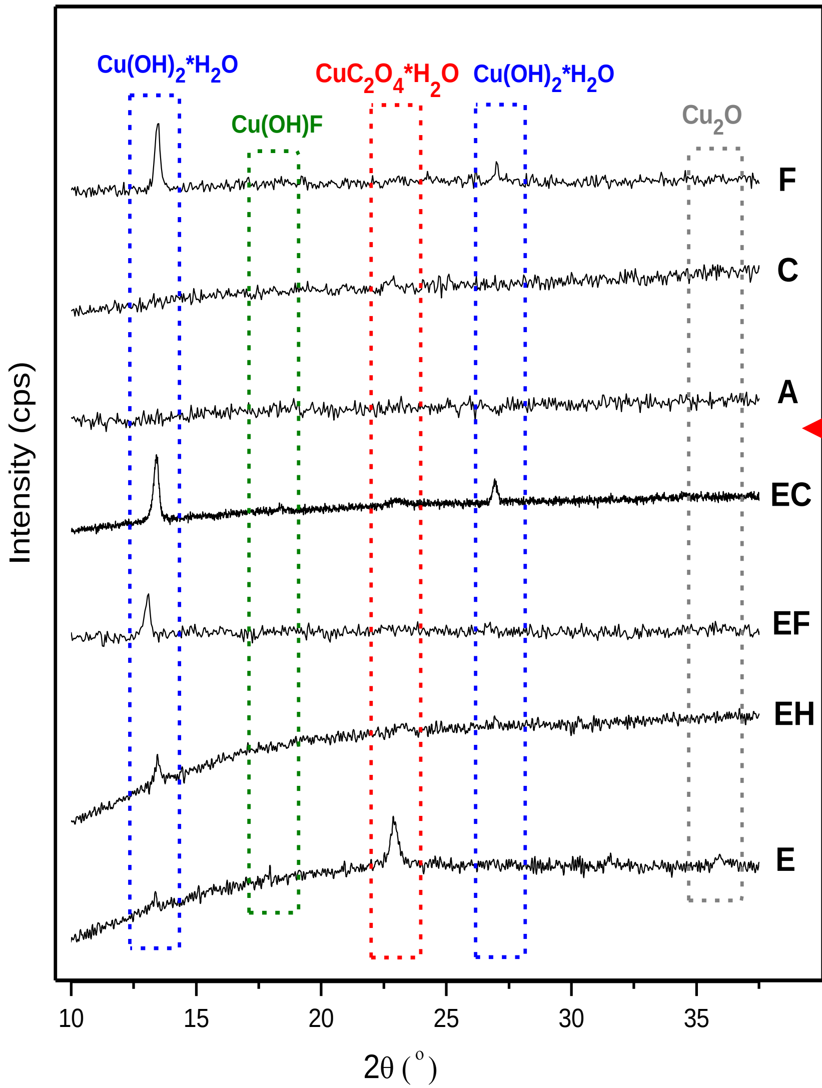
- ***Fourier Transform Infrared Spectroscopy (FTIR)** - Middle range order in crystal and amorphous structures:*

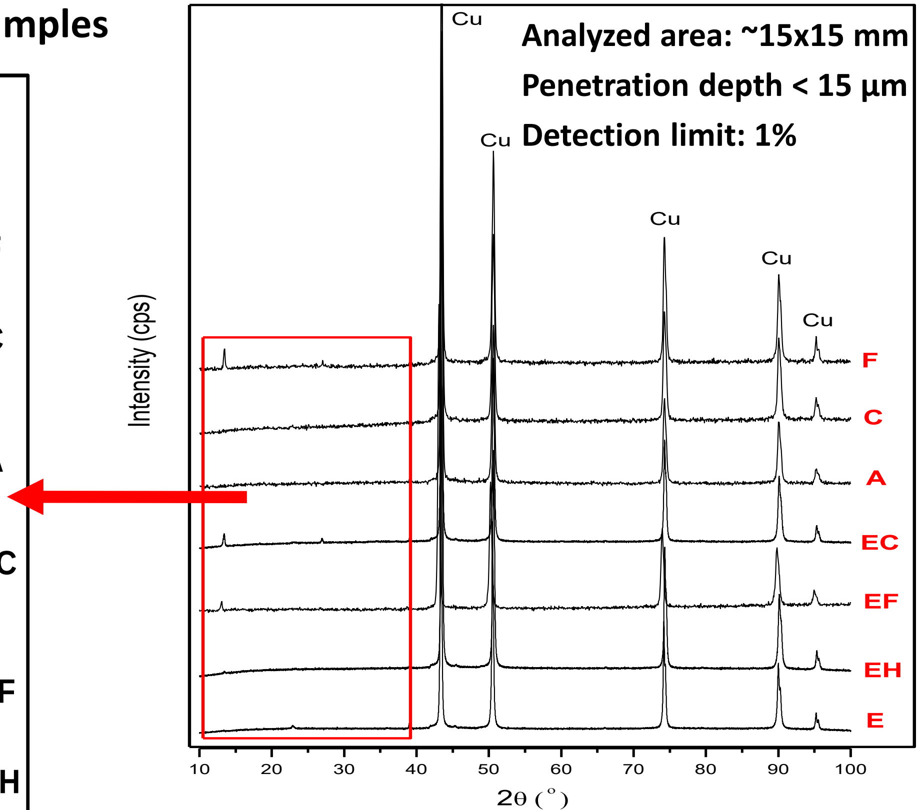
measures interaction of infrared radiation with chemical bonds within a material thus giving information on functional groups within a molecule and energy of chemical bonds (penetration depth 0.5 - 2 µm, detection limit: ~0.1 wt%)

40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

X-ray diffraction analysis: Crystal structure identification

Comparison of XRD patterns of cathode samples





Crystalline deposit on cathode surface

Center E: $CuC_2O_4{*}H_2O$, $Cu(OH)_2{*}H_2O$, Cu(OH)F, Cu_2O

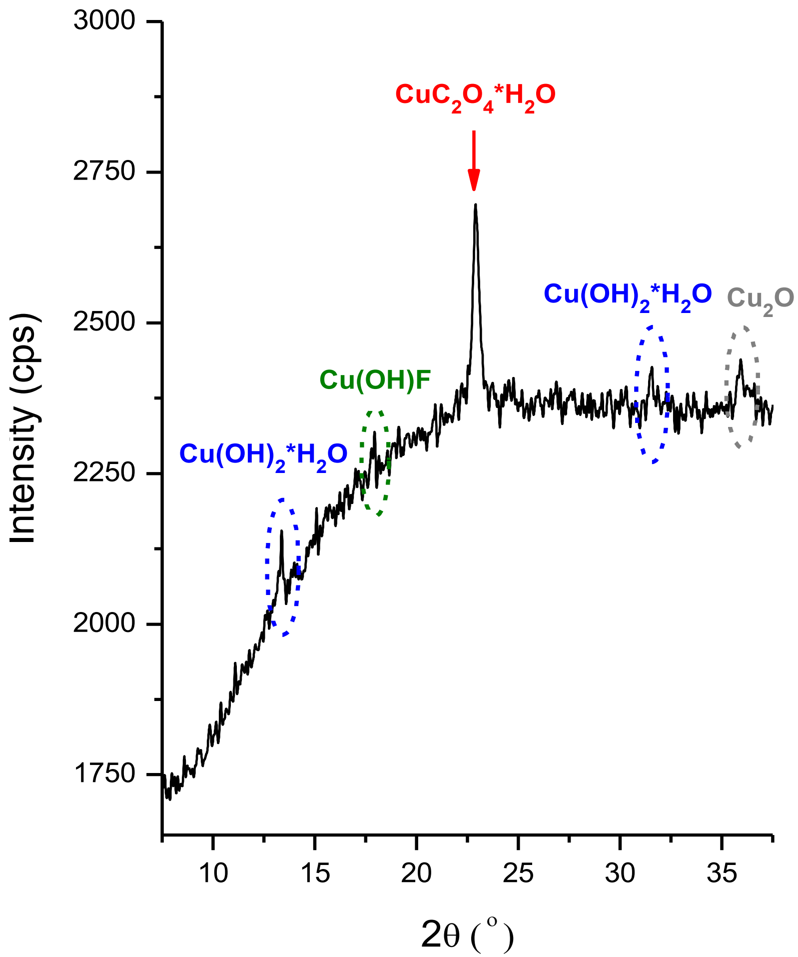
Intermediate 5 cm EH, EF, EC: $Cu(OH)_2{*}H_2O$

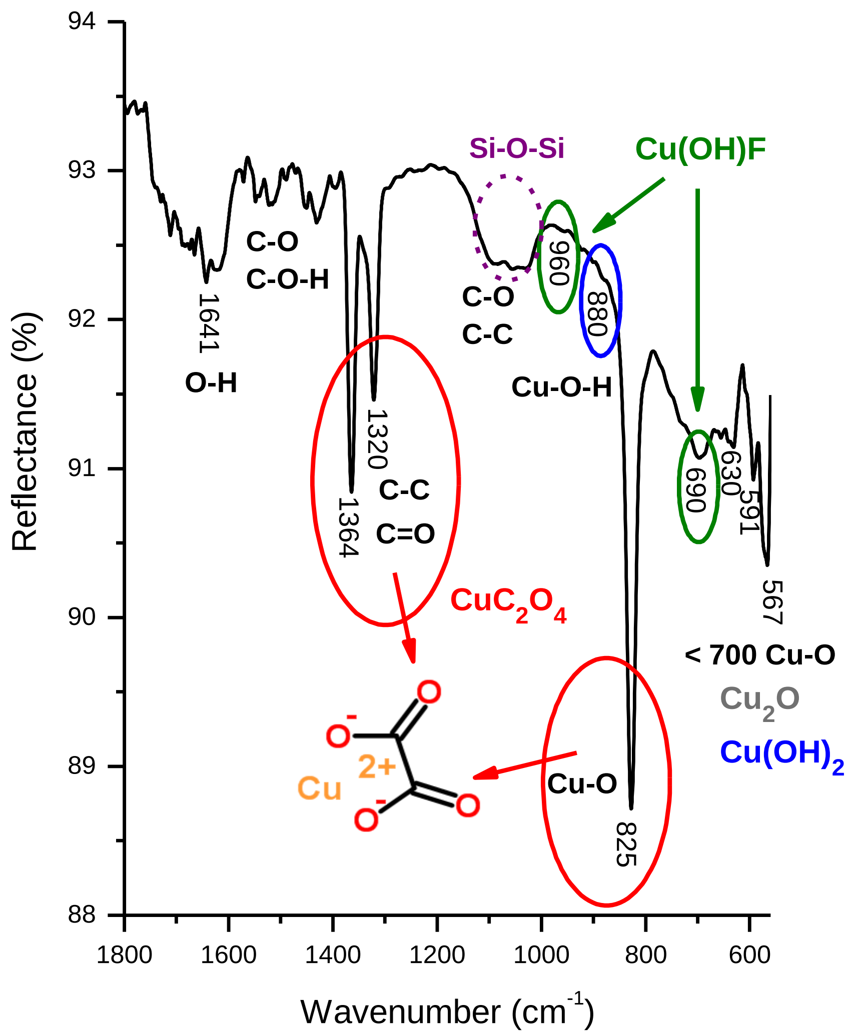
Edge-middle 8 cm F: $Cu(OH)_2{*}H_2O$

Edge-corner 10 cm A, C: No crystalline deposit

40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

Comparison of XRD and IR results for cathode sample E (center of irradiation zone)



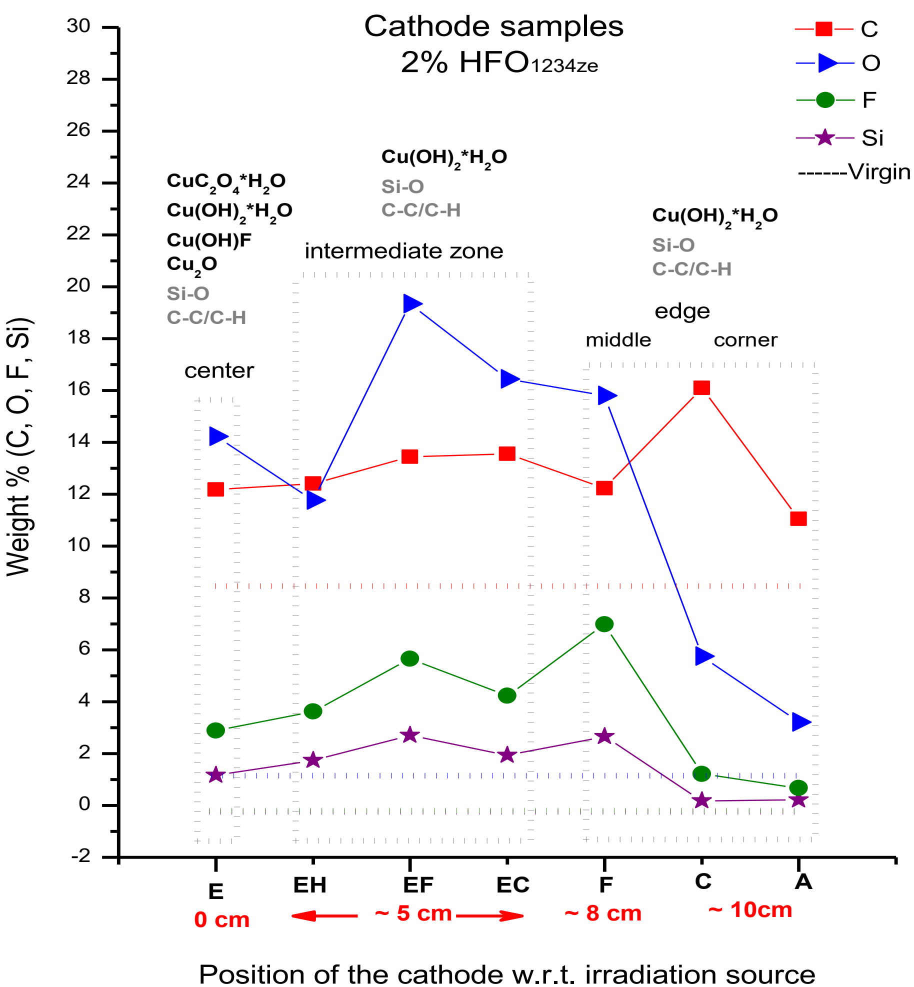


- Dominant crystal phase is $CuC_2O_4*H_2O$
- Crystal phases $Cu(OH)_2*H_2O$, $Cu(OH)F$, Cu_2O are present in lower amount
- Si-O-Si bonds and C-C/C-H bonds indicate presence of amorphous polymers

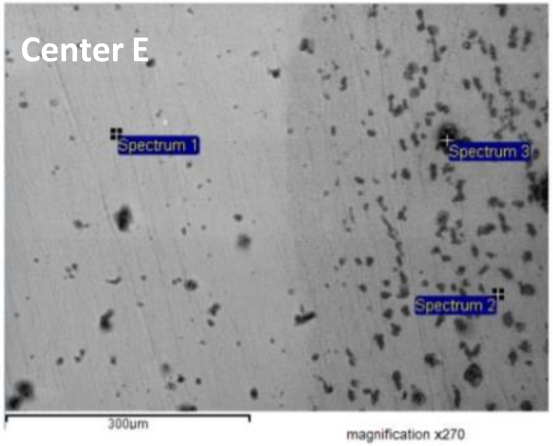
40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

Averaged EDS data of cathodes overlaid with XRD and FTIR results

EDS measurements of every cathode were performed in several regions (~ 1.2x1.2 mm).

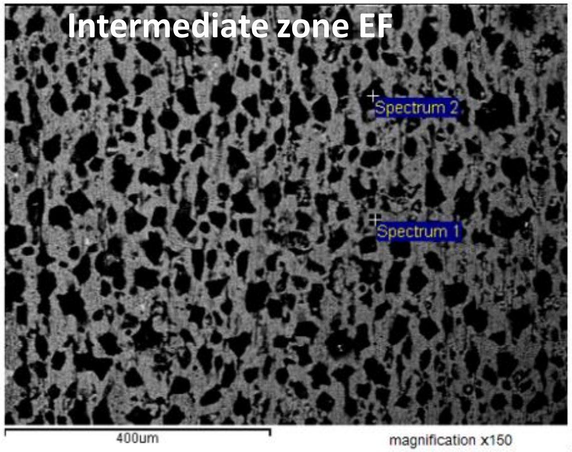


EDS analysis in selected points.



All results in weight%

Spectrum	In stats.	C	O	F	Al	Si	Ca	Cu	Total
Spectrum 1	Yes	7.43	4.79	0.60				87.18	100.00
Spectrum 2	Yes	10.09	11.47	0.86				77.58	100.00
Spectrum 3	Yes	37.09	40.40	4.34	2.38	5.96	2.82	7.02	100.00



All results in weight%

Spectrum	In stats.	C	O	F	Si	Cu	Total
Spectrum 1	Yes	21.07	14.89	2.76	0.56	60.72	100.00
Spectrum 2	Yes	3.25	23.10	27.73	9.41	36.51	100.00

Deposit on the cathode surface:

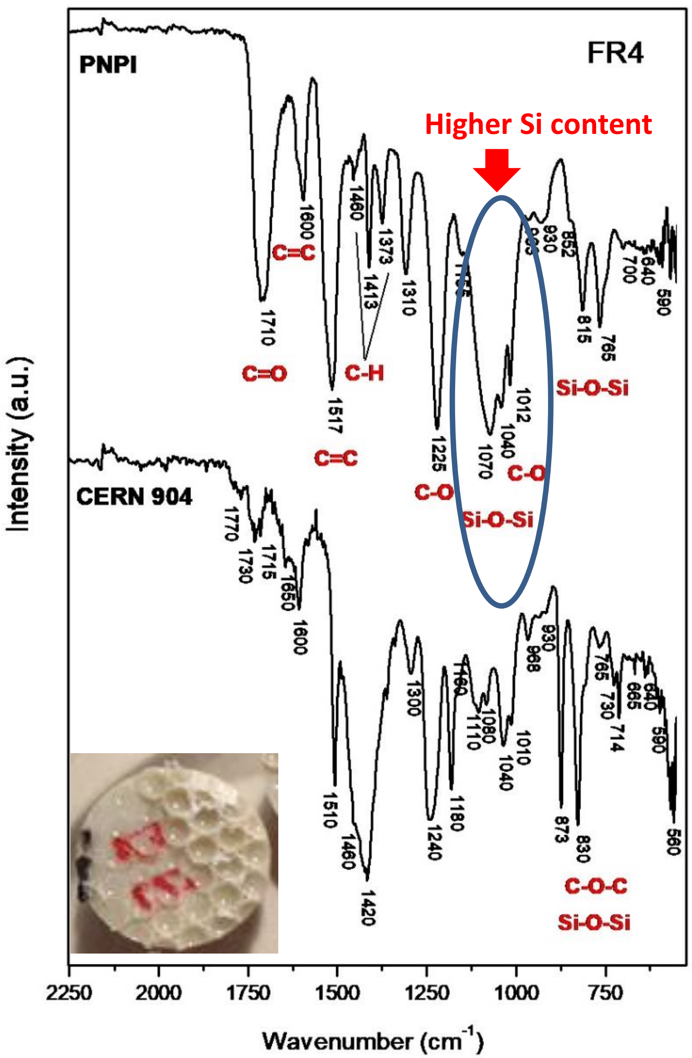
crystalline: $CuC_2O_4*H_2O$, $Cu(OH)_2*H_2O$, Cu(OH)F, Cu_2O

amorphous: Si-O, C-C/C-H, polymers

40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

Analysis of FR4 material

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



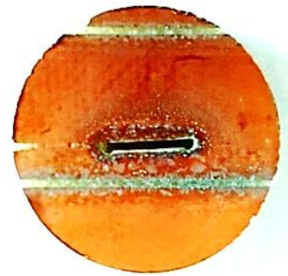
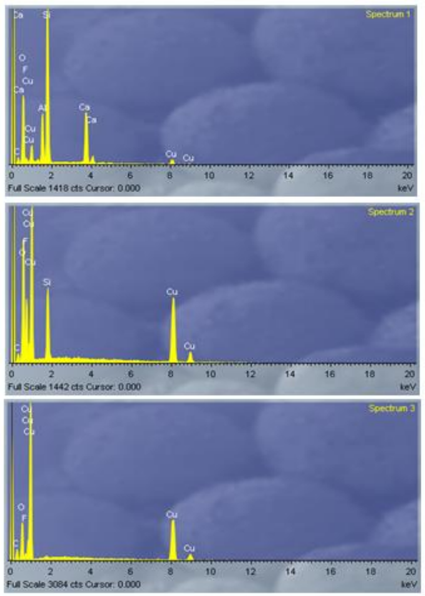


Table 3: Typical constituents of E-Glass [4]

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)



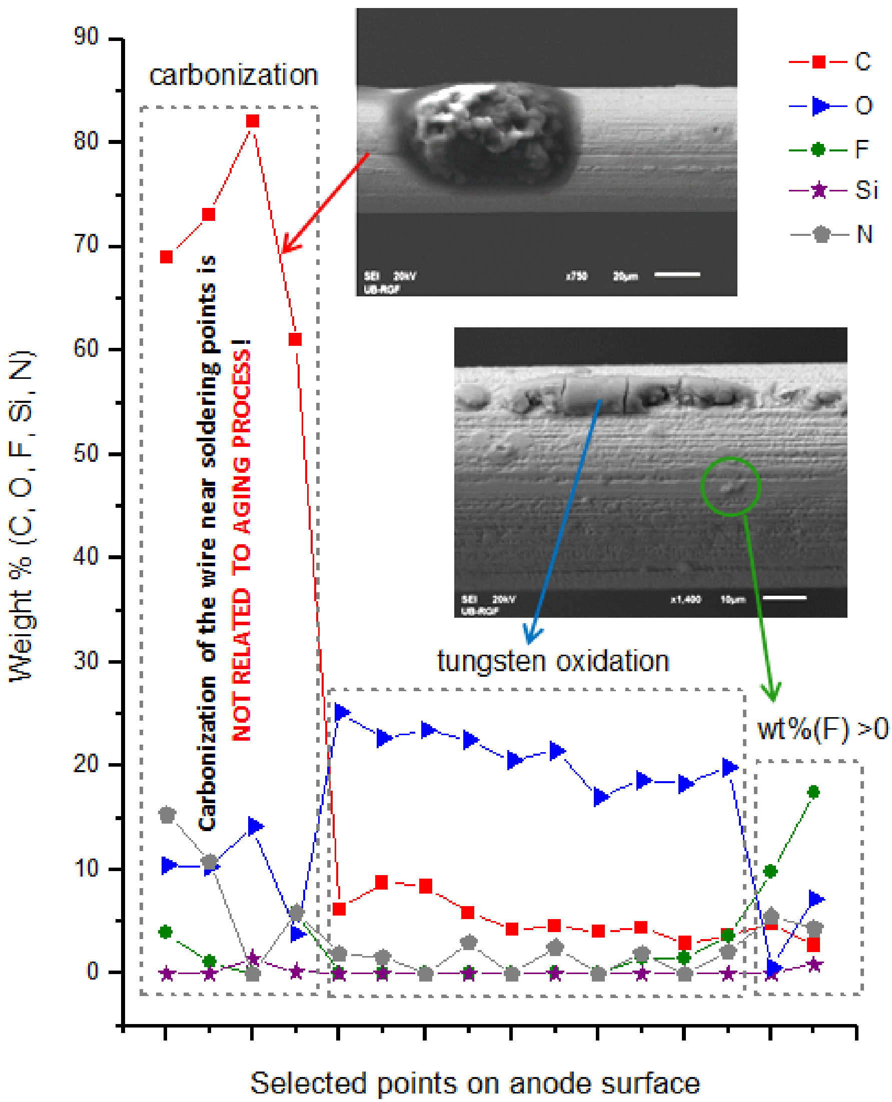
All results in weight%

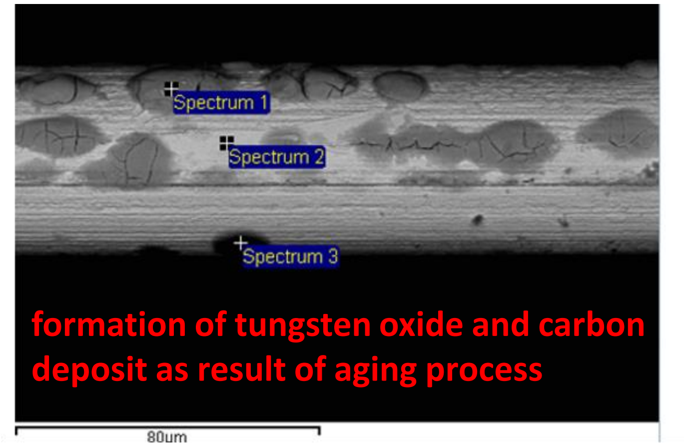
Spectrum	In stats.	C	O	F	Al	Si	Ca	Cu	Total
Spectrum 1	Yes	9.92	41.72	5.47	5.69	20.95	11.45	4.81	100.00
Spectrum 2	Yes	7.04	23.75	20.75		7.02		41.44	100.00
Spectrum 3	Yes	16.64	20.96	3.59				58.81	100.00

Can samples with different FR4 material be compared?

40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

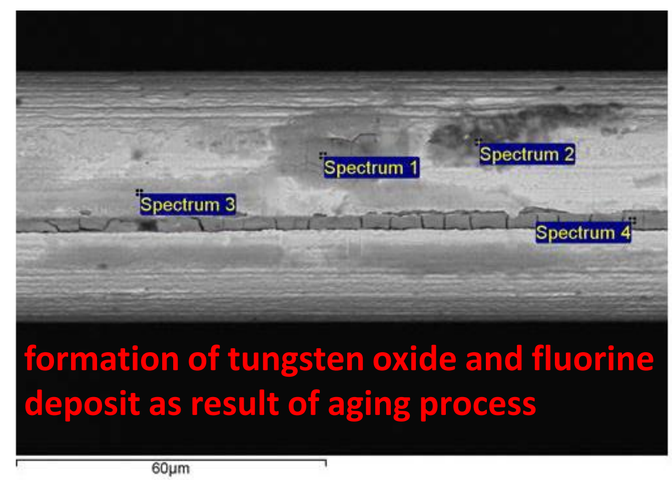
SEM/EDS analysis of anode wire aging





All results in weight%

Spectrum	In stats.	C	N	O	F	Al	Si	Cl	W	Au	Total
Spectrum 1	Yes	4.86	0.00	24.42				0.00	69.83	0.88	100.00
Spectrum 2	Yes	5.61	4.75	1.13				0.00	4.57	83.95	100.00
Spectrum 3	Yes	60.95	5.87	3.85	5.86	0.71	0.21	0.69	0.37	21.47	100.00

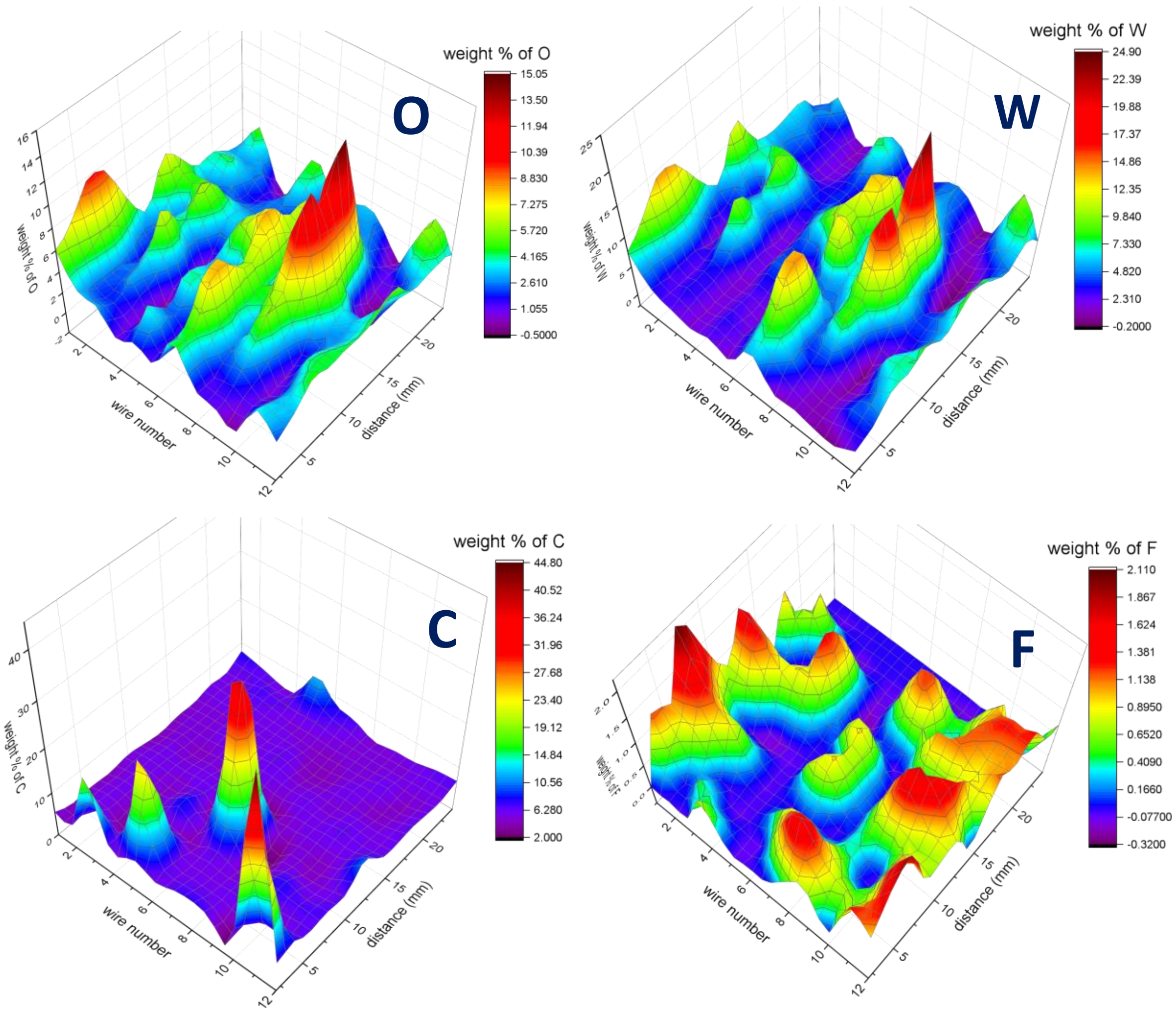


All results in weight%

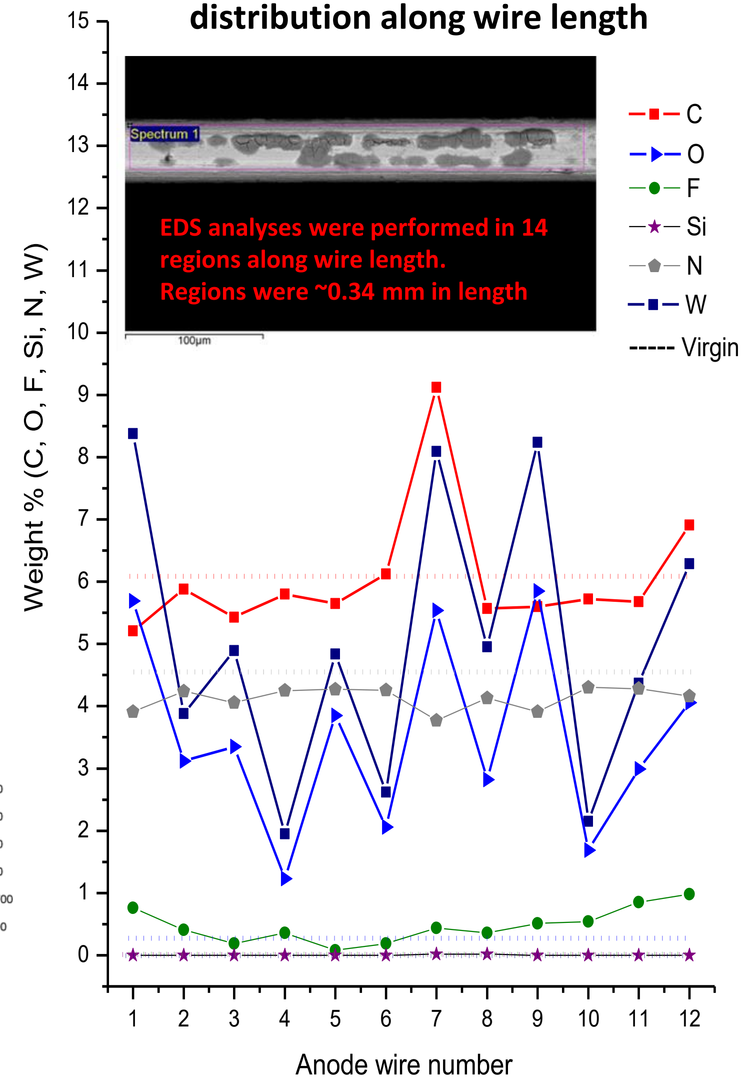
Spectrum	In stats.	C	N	O	F	Si	W	Au	Total
Spectrum 1	Yes	4.52	2.62	22.14	0.00	0.00	45.55	25.17	100.00
Spectrum 2	Yes	2.14	5.08	13.31	19.61	0.00	46.26	13.59	100.00
Spectrum 3	Yes	3.77	3.34	18.93	0.93	0.00	28.85	44.18	100.00
Spectrum 4	Yes	3.55	0.00	19.22	0.00	0.00	71.74	5.49	100.00

40% Ar + 58% CO_2 + 2% HFO1234ze Tests (1.2 C/cm)

EDS results for 12 anode wires
3D Graphs: Elemental distribution across wire length



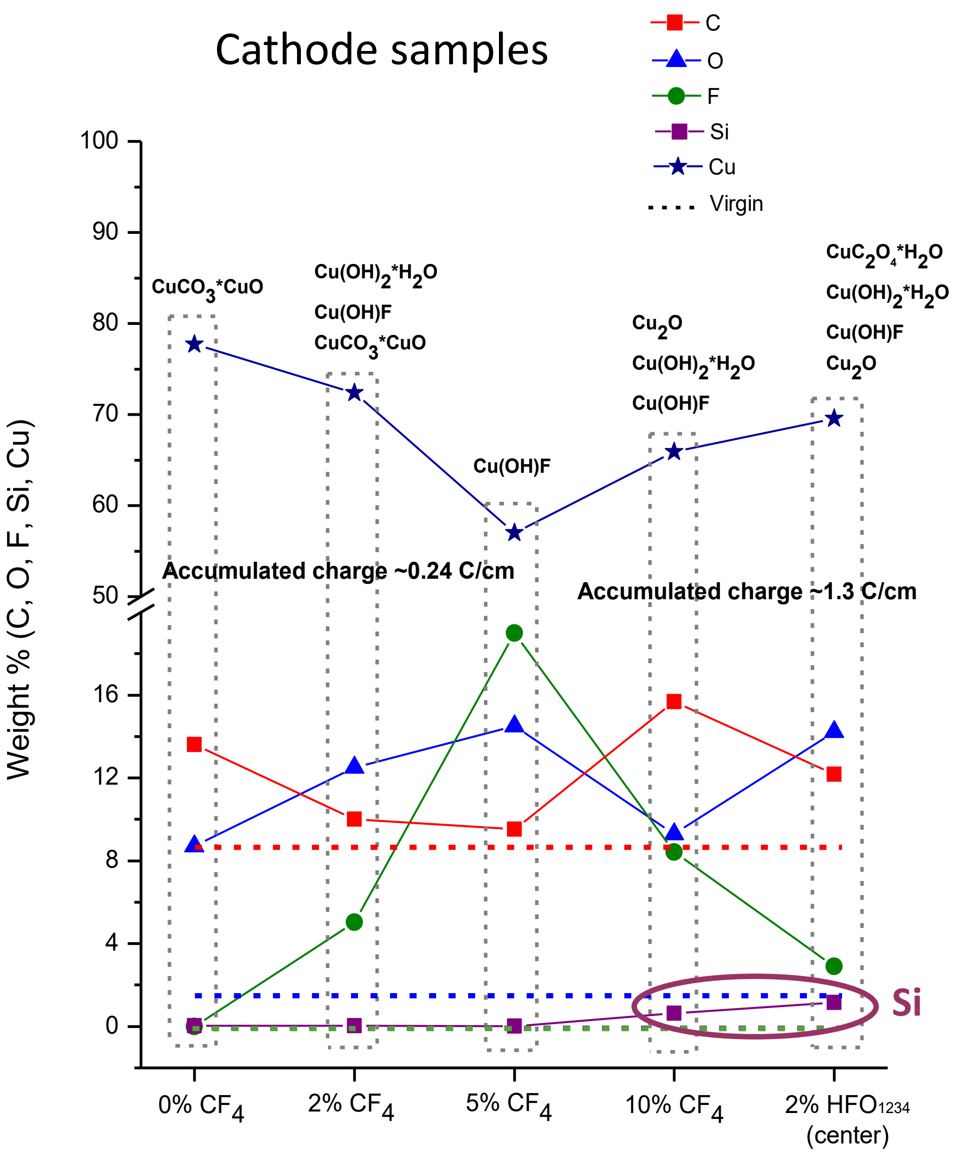
Averaged EDS results for elemental distribution along wire length

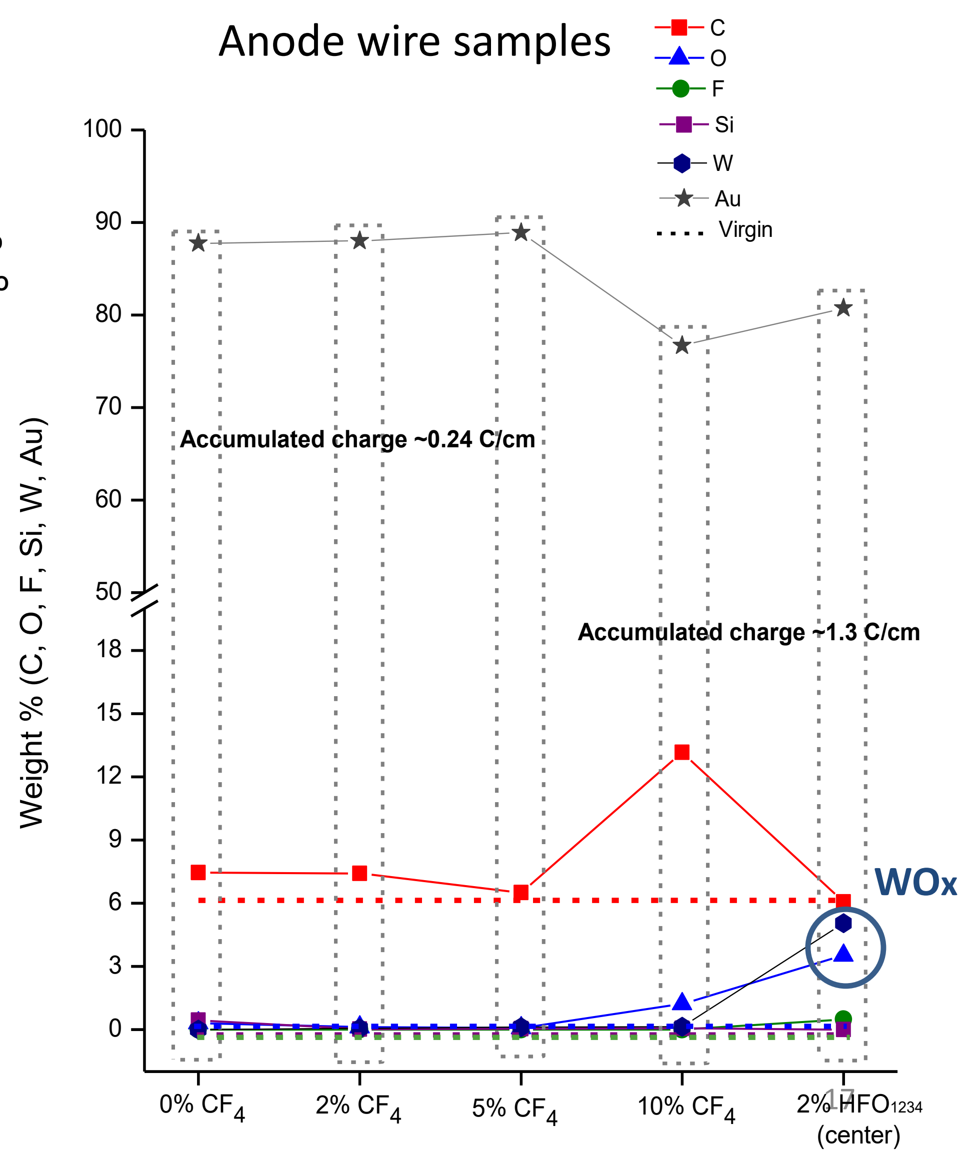


- *Comparable distribution trend of O and W on the wire surface indicate formation of tungsten oxide*
- *C and F deposit on the wire surface is close to reference value -virgin wire sample*

Summary

Comparison of results for irradiated cathode and anode 0, 2, 5 ,10% CF_4 and 2% HFO1234ze (center - E)





HFO_{1234ze} Tests (1.2 C/cm)

Summary of the results

Cathode plates:

- Formation of type of deposit depends on the position of the samples w.r.t. radiation source:

center:

$CuC_2O_4*H_2O$**,** $Cu(OH)_2*H_2O$, $Cu(OH)F$ and Cu_2O (**crystal**)
some Si-O and C-C /C-H bonds (**amorphous**)

5 and 8 cm from the center:

$Cu(OH)_2*H_2O$ (**crystal**), some Si-O and C-C /C-H bonds (**amorphous**)

10 cm from the center:

no crystalline deposit, some Si-O and C-C /C-H bonds (**amorphous**)

Anode wires:

- Carbon deposit on anode wires is close to reference value - virgin wire sample
- **Formation of tungsten oxide is detected in significant amount.**

Despite the deposit on electrode surface, no gas gain reduction was seen during the tests, ***but*** *significant increase of the dark current was observed – need to study this problem!*

Conclusion

Comparison of results for CF_4 and HFO1234ze tests

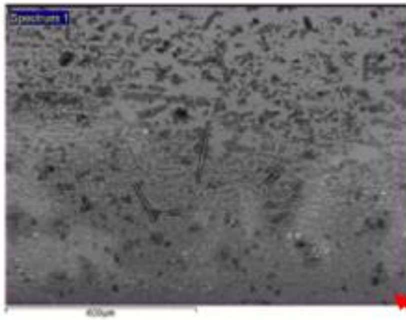
- Anode wire aged in gas mixture containing **5% CF_4** (accum. charge 0.24 C/cm) showed **no silicon deposit** and the **lowest amount of carbon** deposit (close to reference - virgin wire ~ 0.5 wt% higher), compared to 10, 2 and 0 % CF_4 trials.
- **No** formation of **tungsten oxide** on anode wires was detected for **CF_4** trials.
- **HFO1234ze** tests are characterized with formation of **significant amount of tungsten oxide** on anode wires, while **carbon** deposit is close to reference value - virgin wire sample.
- *Higher amount of **silicon** is detected on the cathode samples with FR4 material containing more fiber glass. Two different types of the cathode planes were used during the mini CSC construction.*

Main difference regarding wires between CF_4 and HFO1234ze tests: formation of tungsten oxide in the presence of HFO1234ze

Backup slides

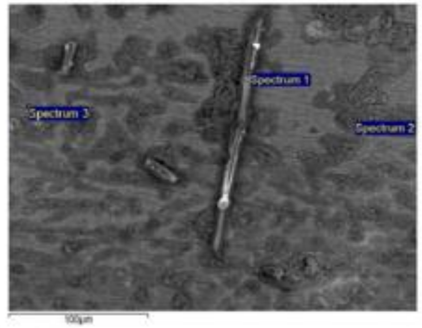
HFO1234ze Tests

EDS analysis: Cathode E (center) - Analyzed areas ~ 1.2x1.2 mm, magnification x100



All results in weight%

Spectrum	In stats.	C	N	O	F	Al	Si	Cl	Ca	Cu	Total
Spectrum 1	Yes	14.05	0.00	28.06	9.19	0.33	4.62	0.23	0.28	43.23	100.00



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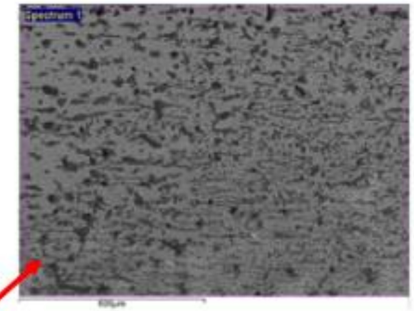
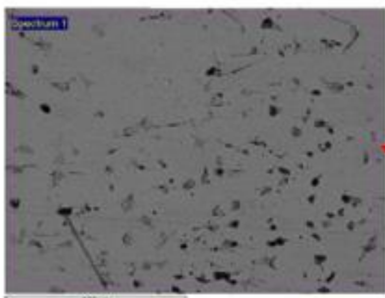


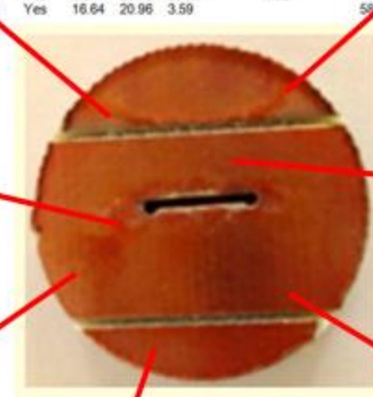
All results in weight%

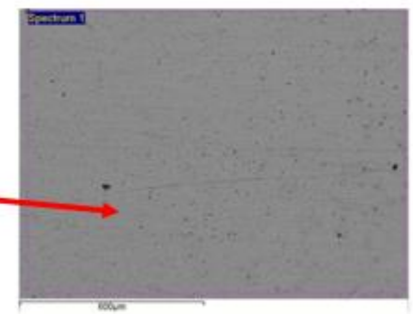
Spectrum	In stats.	C	N	O	F	Al	Si	Cl	Ca	Cu	Total
Spectrum 1	Yes	13.32	0.00	23.44	8.41	0.53	3.74	0.24	0.31	49.99	100.00



All results in weight%

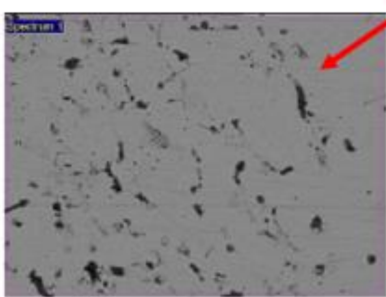
Spectrum	In stats.	C	N	O	F	Si	Cl	Cu	Total
Spectrum 1	Yes	11.68	0.00	12.01	1.44	0.66	0.00	74.21	100.00





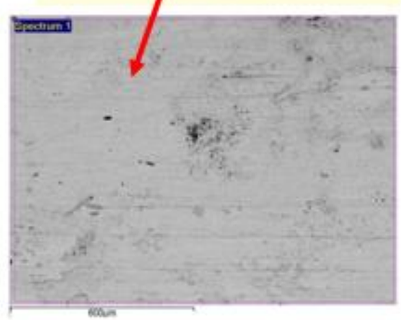
All results in weight%

Spectrum	In stats.	C	O	F	Si	Cu	Total
Spectrum 1	Yes	10.73	9.51	2.11	0.37	77.28	100.00



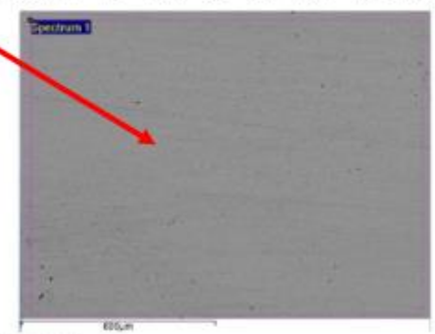
All results in weight%

Spectrum	In stats.	C	N	O	F	Si	Cl	Cu	Total
Spectrum 1	Yes	11.01	0.00	11.45	1.42	0.78	0.00	75.34	100.00



All results in weight%

Spectrum	In stats.	C	O	F	Si	Cu	Total
Spectrum 1	Yes	12.52	11.86	1.10	0.32	74.21	100.00

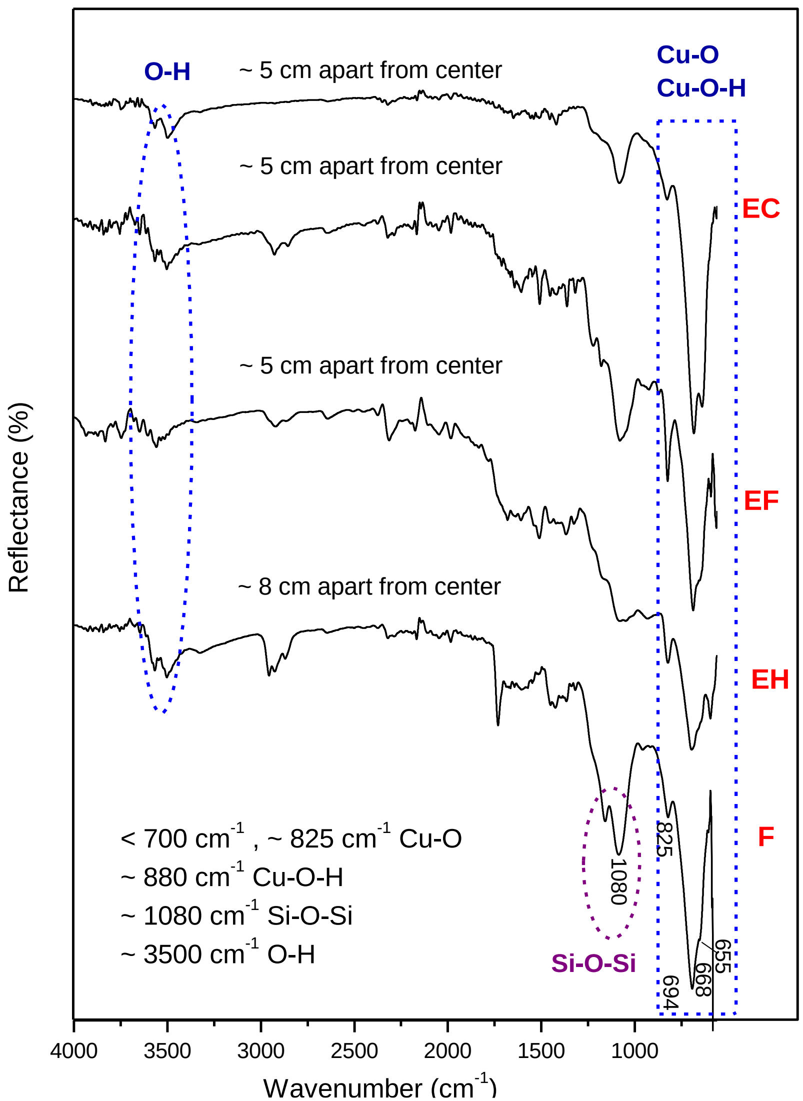


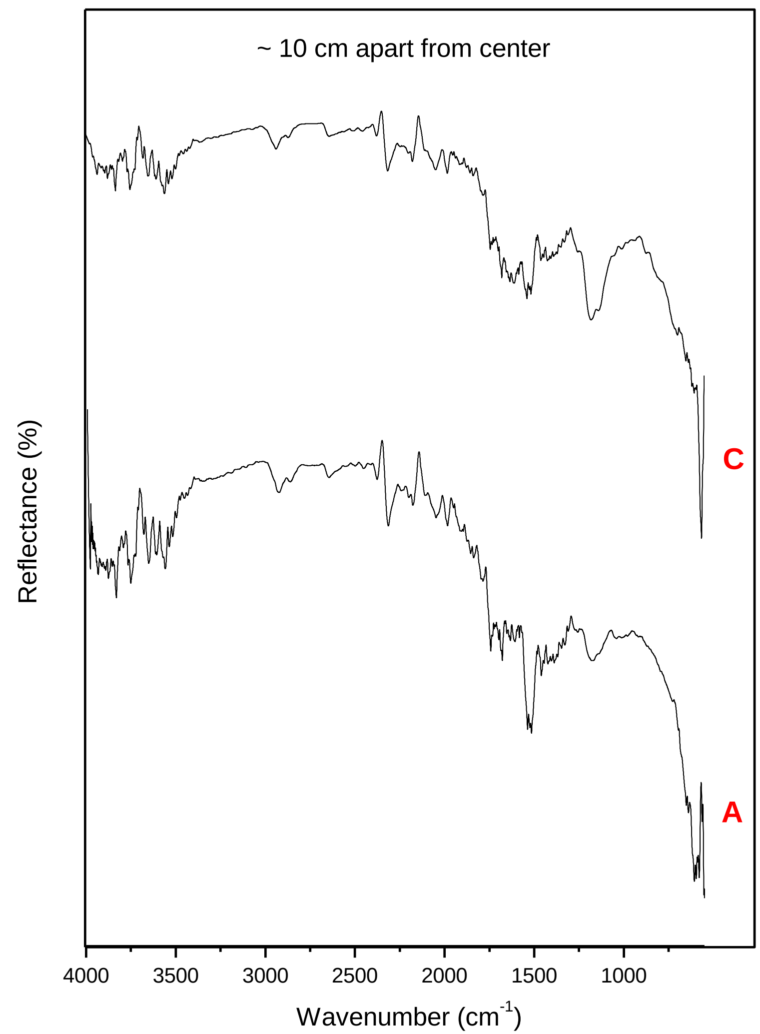
All results in weight%

Spectrum	In stats.	C	N	O	F	Si	Cl	Cu	Total
Spectrum 1	Yes	11.33	0.00	10.16	1.06	0.00	0.00	77.46	100.00

HFO_{1234ze} Tests

IR spectra of cathode samples: 5, 8 and 10 cm apart from the irradiation center

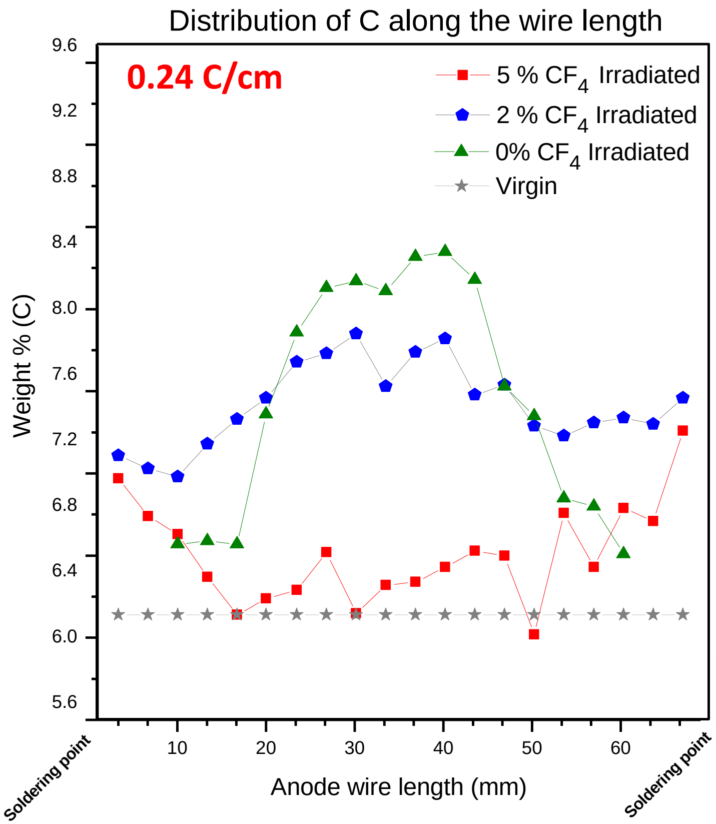




IR results: $Cu(OH)_2*H_2O$ compound, Si-O-Si bonds and C-C/C-H bonds

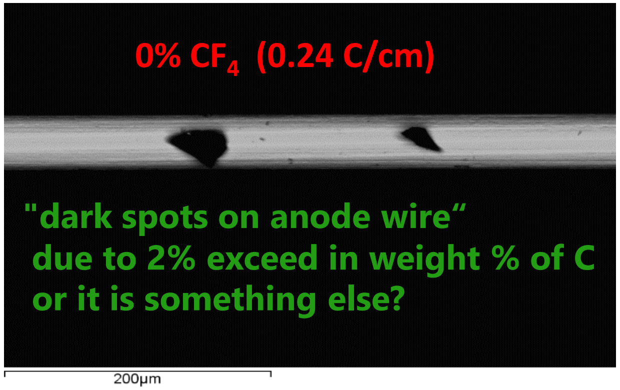
CF_4 Tests

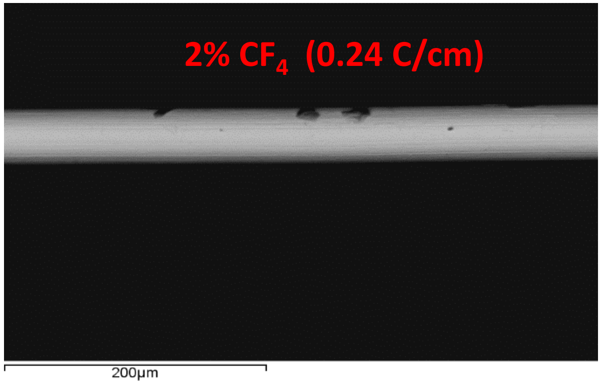
Microscopic analysis and distribution of carbon along anode wire length 0, 2 and 5 % CF4

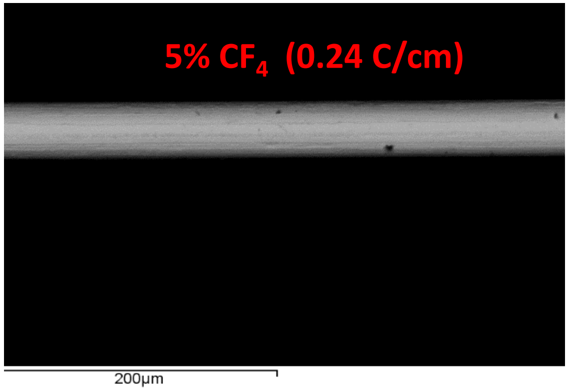


Darkening of the wires: C deposit or mechanical damage?

Backscattered electron composition images - 2D

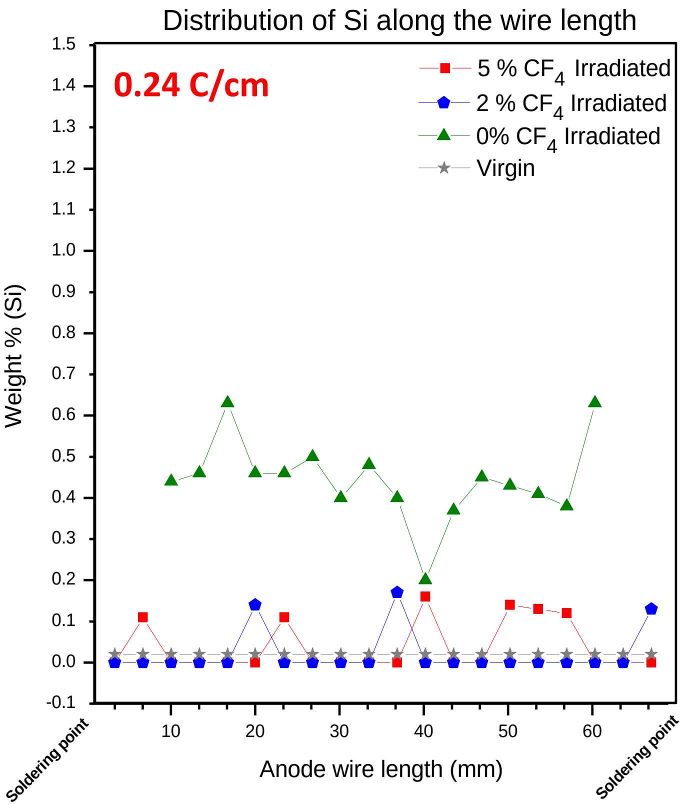


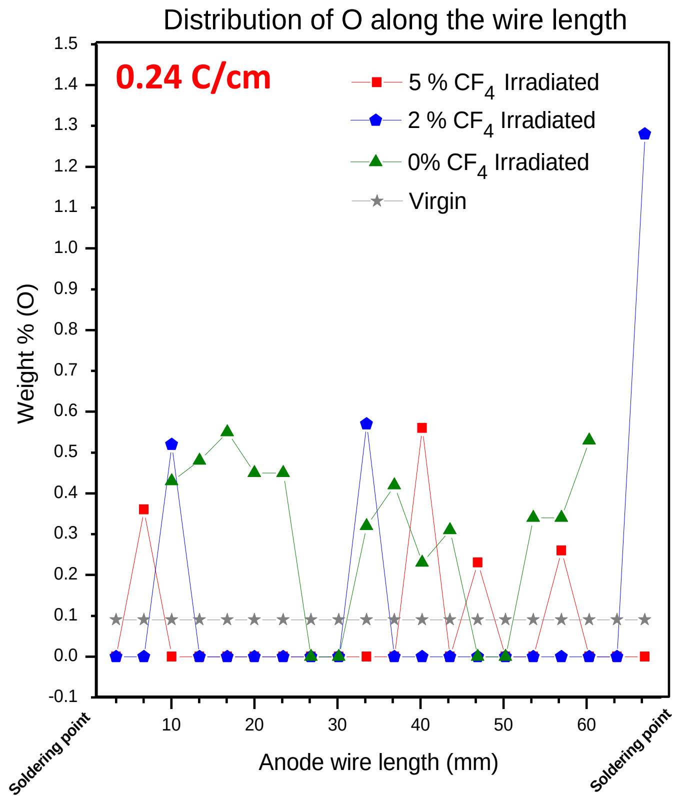




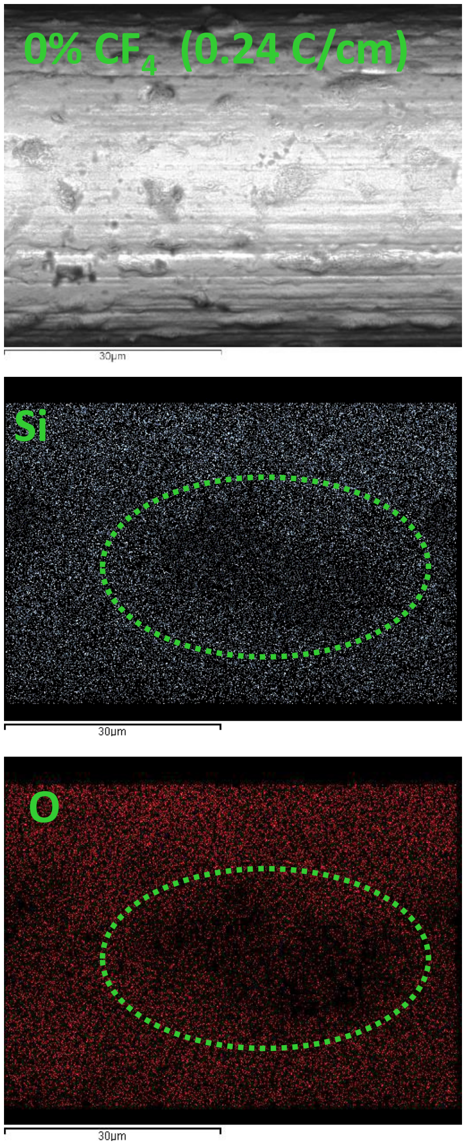
CF_4 Tests

EDS distribution of Si and O along anode wire length
0, 2 and 5% CF_4, 0.24 C/cm





Elemental mapping of Si and O
0 % CF_4, 0.24 C/cm



- Si deposit is observed on anode wire after ageing in 40% Ar + 60% CO_2 + 0% CF_4
- Comparable distribution trend of Si and O on wire surface indicate formation of Si-O based polymers

CF_4 in gas mixture is cleaning the wire from Si-O based polymers