DE LA RECHERCHE À L'INDUSTRIE

The impact of trace amounts of NH_3, HCl and $C_4Cl_4F_6$ in hydrogen on FC performance

I. Profatilova[1],F. Fouda-Onana[1], M. Heitzmann[1],
T. Bacquart[3], A. Rojo Esteban[2], P.-A. Jacques[1]

[1]Atomic Energy and Alternative Energies Commission (CEA), LITEN, Grenoble, France
[2]CEM Spanish Metrology Center, Madrid, Spain
[3]National Physical Laboratory, Teddington, UK

HYDROGEN project: Final meeting
***21st May,** 2019*

www.cea.fr

INTRODUCTION

The following impurities in H_2 were investigated: NH_3, HCL and $C_4Cl_4F_6$.

Present requirements for H_2 quality ISO/DIS 14687:2018(E):

→**Total halogenated compounds content is <0.05 µmol/mol** (halogen ion equivalent, all halogenated compounds which could potentially be in the hydrogen gas)
→**NH_3 is <0.1 µmol/mol**

Possible sources of NH_3, HCl and $C_4Cl_4F_6$ for fuel cells:

→ From ambient air (cross-over from the cathode side)
→ H_2 production: chlor-alkali plants (in case of failure of purification)
→ $C_4Cl_4F_6$ was found in H_2 from refueling station *(Int. J. Hydrogen Energy 37 (2012) 1770 and HyCoRa project results (2015-2017)*.

NH_3 and HCl in trace concentrations on FC performance are poorly investigated especially over long term

No available data in literature regarding the inpact of $C_4Cl_4F_6$ on FC performance.

ISO 14687-2; O.A. Baturina et al., J. Electrochem. Soc. 161 (2014) F365.

OBJECTIVES OF THE WORK

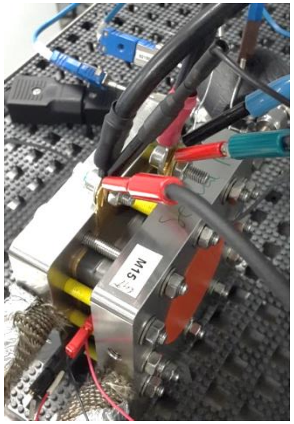
- **Understand and quantify the impact of low concentrations of NH_3, HCl and $C_4Cl_4F_6$ in fuel on PEM FC performance under dynamic automotive load cycling;**

- **Propose a mechanism for PEMFC components degradation in presence of the impurities;**

- **Give recommendations to ISO on acceptable concentrations of the three impurities in H_2 for PEMFC.**

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Single cell tests: Experimental setup

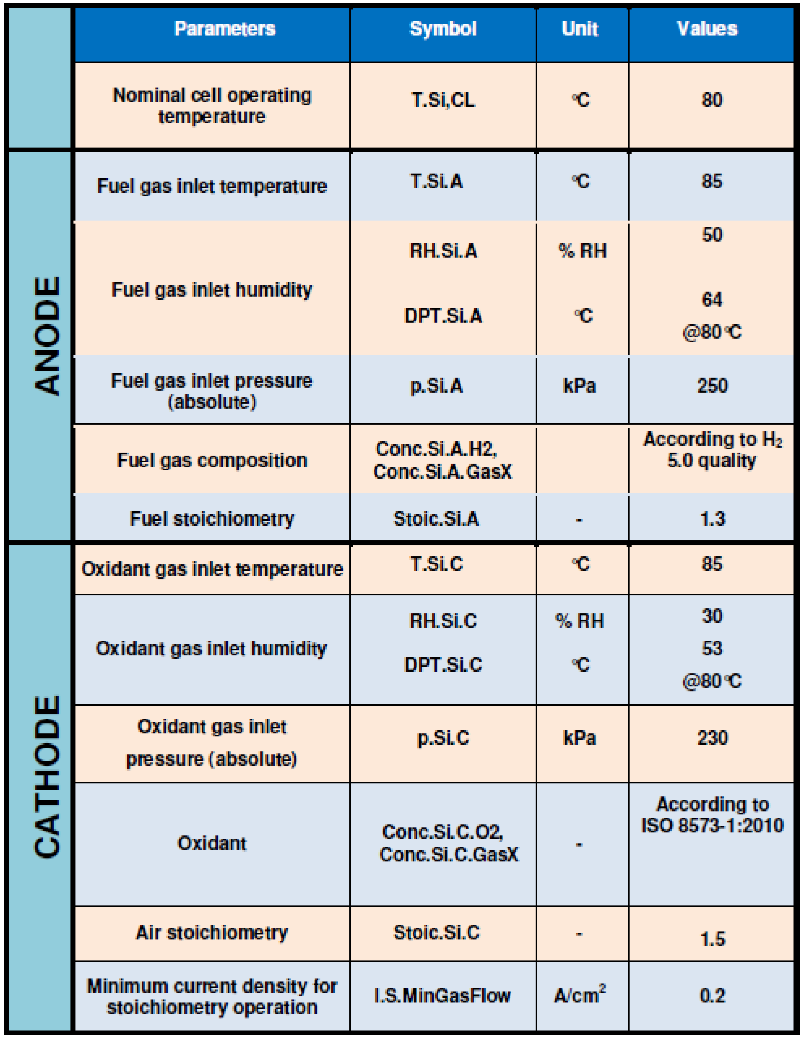


25 cm^2 single cell

Test bench with sulfinert pipes

MEA characteristics	
Anode Pt loading, mg/cm^2	**0.11**
Cathode Pt loading, mg/cm^2	**0.34**
Membrane	**Gore**
Fuel used	**H_2 pure (ref),** **H_2 + 2 ppm NH_3** **H_2 +0,2 ppm HCl** **H_2 + 0,2 ppm $C_4Cl_4F_6$**

European harmonized FC automotive conditions :



	Parameters	Symbol	Unit	Values
	Nominal cell operating temperature	T.Si,CL	°C	80
ANODE	Fuel gas inlet temperature	T.Si.A	°C	85
	Fuel gas inlet humidity	RH.Si.A DPT.Si.A	% RH °C	50 64 @80°C
	Fuel gas inlet pressure (absolute)	p.Si.A	kPa	250
	Fuel gas composition	Conc.Si.A.H2, Conc.Si.A.GasX		According to H_2 5.0 quality
	Fuel stoichiometry	Stoic.Si.A	-	1.3
CATHODE	Oxidant gas inlet temperature	T.Si.C	°C	85
	Oxidant gas inlet humidity	RH.Si.C DPT.Si.C	% RH °C	30 53 @80°C
	Oxidant gas inlet pressure (absolute)	p.Si.C	kPa	230
	Oxidant	Conc.Si.C.O2, Conc.Si.C.GasX	-	According to ISO 8573-1:2010
	Air stoichiometry	Stoic.Si.C	-	1.5
	Minimum current density for stoichiometry operation	I.S.MinGasFlow	A/cm^2	0.2

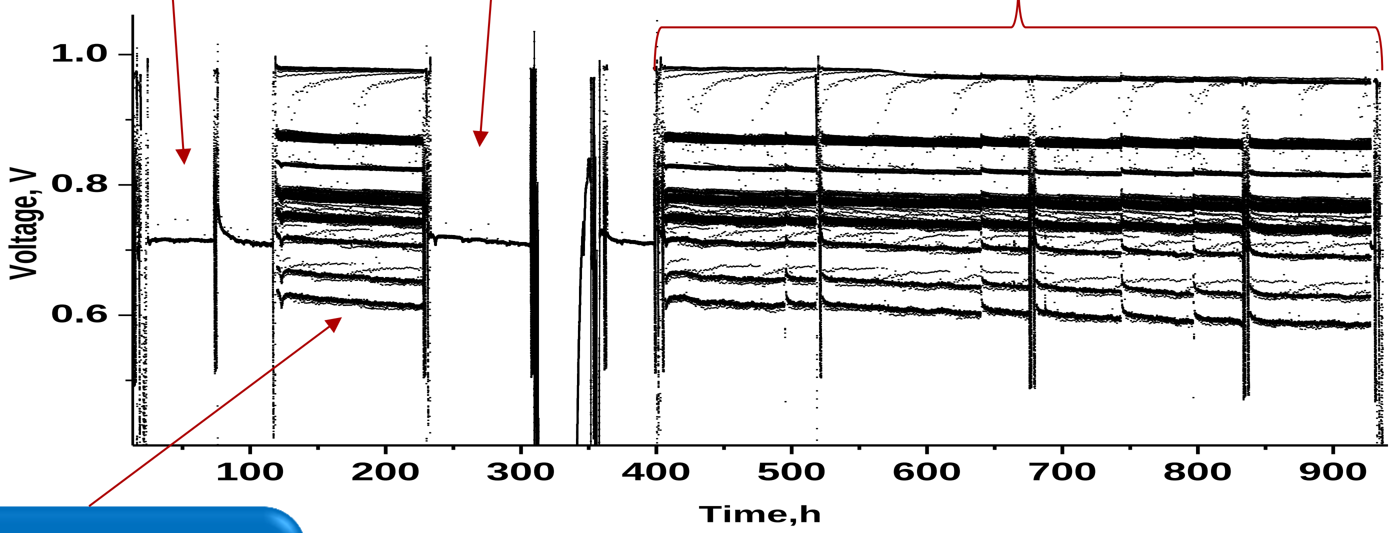
doi:10.2790/54653

EXAMPLE OF VOLTAGE PROFILE FOR REFERENCE TEST

Stationary test 1 @ 0.6 A/cm^2 for 48 h + electrochemical characterization

Stationary test 2 @ 0.6 A/cm^2 for 72 h + electrochemical characterization

NEDC cycling test for 500 h + electrochemical characterization



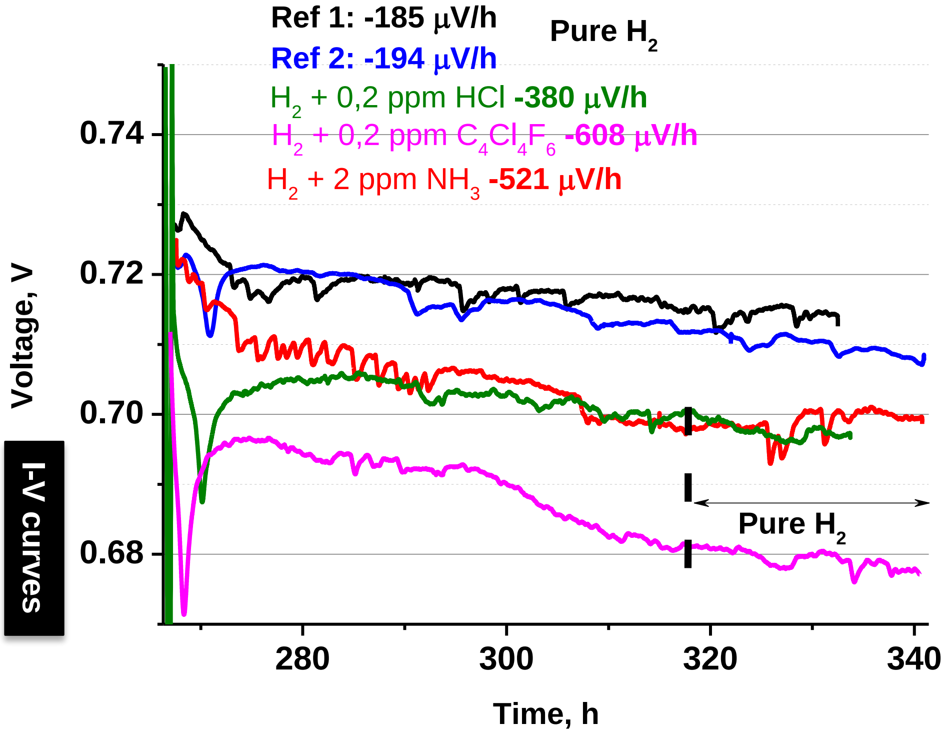
NEDC cycling test for 100 h + electrochemical characterization

<u>Electrochemical characterization and purification protocol:</u>

- 2 Polarization curves (overall cell performance);
- CVs cathode and anode (100 % RH, ECSA);
- Operation in neat H_2;
- Polarization curve after purification.

STATIONARY 2 PHASE VOLTAGE PROFILES

0.6 A/cm² voltage ageing profile



- **Last 24 h of the test was done in pure H_2 (low RH) → no visible performance recovery:**

I-V curves

6h pure H_2
100 RH

CVs cathode and anode

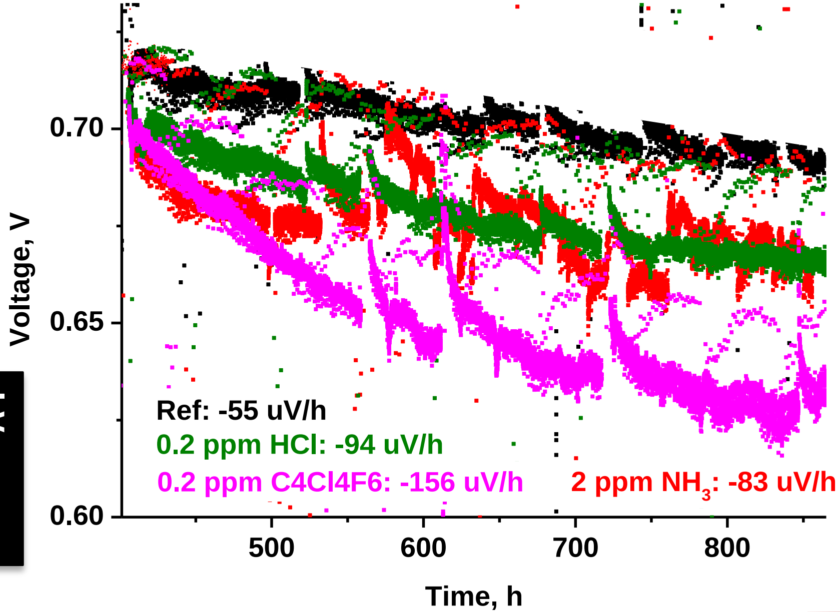
I-V curves

Non-recoverable degradation rate estimation via polarization curves

NEDC TEST FOR 500 H

Extracted at 0.6 A/cm^2 from NEDC profile

I-V curves



I-V curves

CVs cathode and anode

36 h in pure H_2

I-V curves

- **The lowest total degradation rate was observed for the cell operated in pure H_2;**

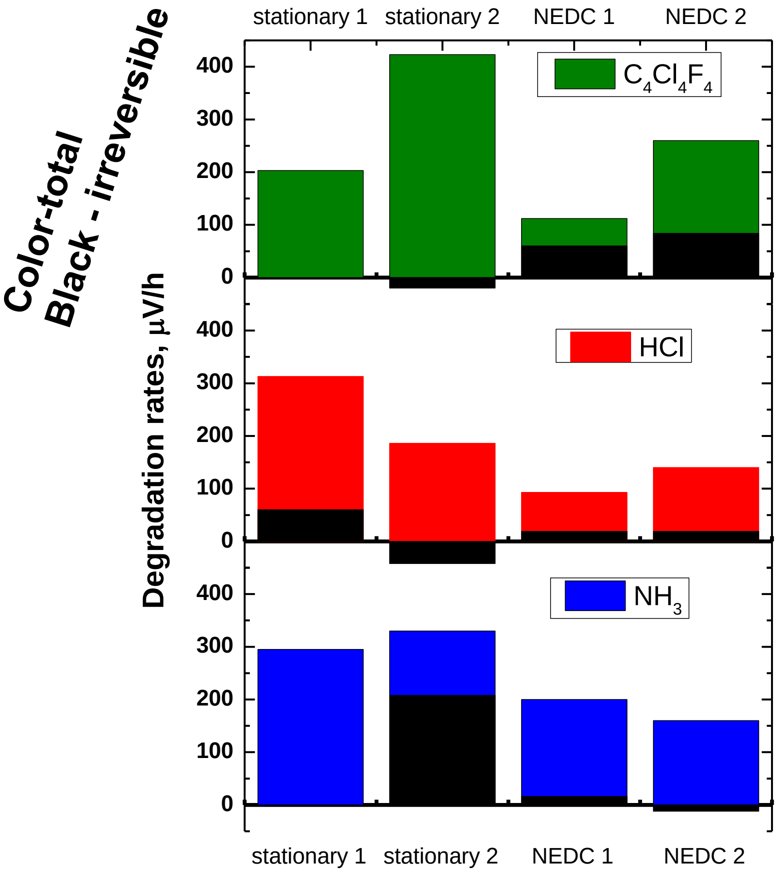
Non-recoverable degradation rate estimation

	Reference	0,2 ppm HCl	0,2 ppm $C_4Cl_4F_6$
Irrevers. degradation rate @ 0.6 A/cm^2, µV/h	-19	-38	-103

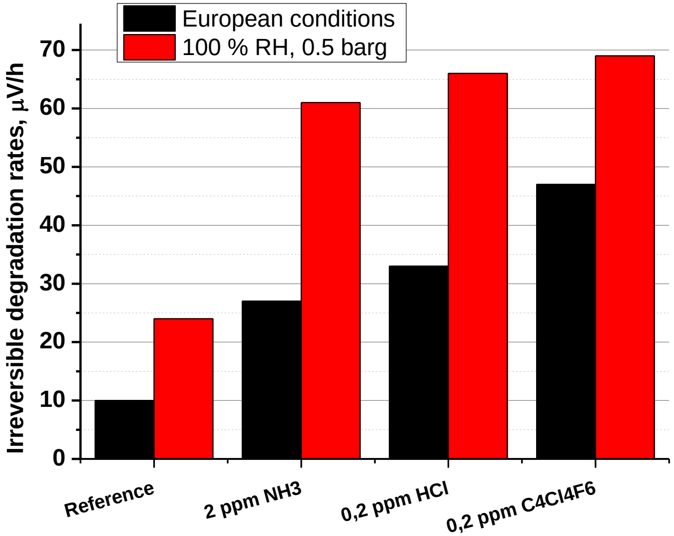
Irina Profatilova – 21st May 2019, HYDROGEN final meeting, Delft, Netherlands

IMPURITY-INDUCED VOLTAGE DEGRADATION

Performance degradation induced by impurities in H_2 in 50-h time scale



Irrecoverable performance degradation in H_2 in 900-h time scale @0,6 A/cm²



- ➢ **Less impact** of contaminants on FC under **dynamic load** compared to stationary operation**;**
- ➢ **The largest part of losses is recoverable;**
- ➢ $C_4Cl_4F_6$ gave the highest FC degradation at a long-term test.

EFFICIENCY OF CLEANING TECHNIQUES

Technique	Impact on FC performance	
2-3 polarisation curves	More impact in case of halogenated impurities	✓
CVs	Small effect	
Operation in pure H_2 low RH (24-30 h)	Low impact	
Operation in pure H_2 100 % RH (6-40 h)	The highest performance recovery, but no total recuperation. More efficient for NH_3 compared to pol. curves	✓ ✓

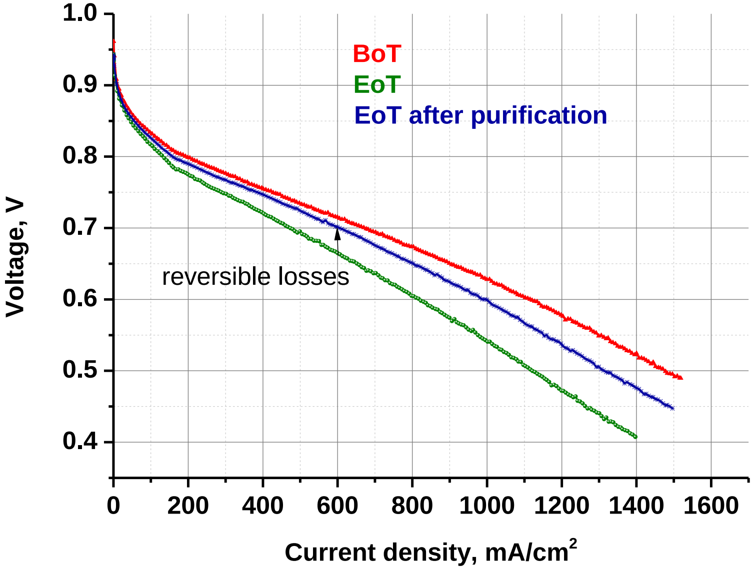
Calculations of acceptable impurities concentrations in H_2

H_2 IMPURITY CONTENT THRESHOLD CALCULATIONS

Calculations are done based on the polarization curves taken at BoT and EoT (after purification: operation in pure H_2 40h and CVs) @ 0.6 A/cm^2.

DOE Technical target 2020: 5000 h with <10% rated power loss.

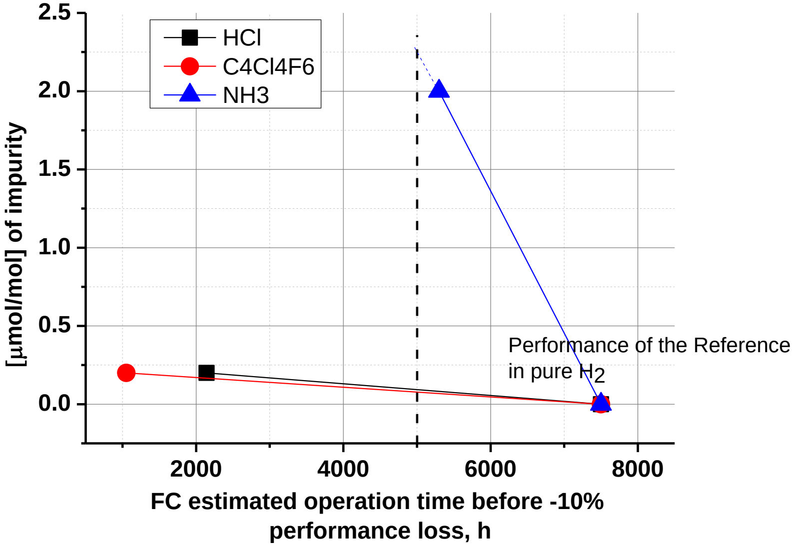
Example of polarization curves for H_2 + 2 ppm NH_3



-1.8% performance loss in 954h

-10% loss in 5300h if linear.

Calculation of impurity content threshold based on linear degradation rate assumption



Simple linear extrapolation of the impurity concentrations to 5000h.

Very approximate method

THRESHOLDS FOR IMPURITIES CONTENT IN H_2

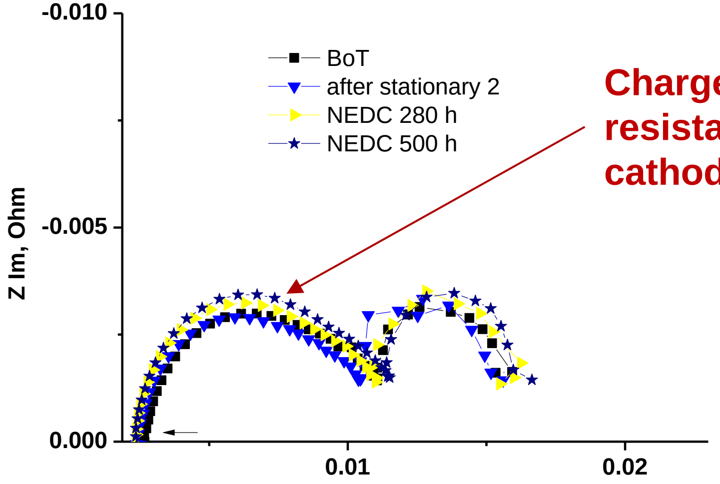
Impurity in H_2	[µmol/mol], taken for study in FC	Threshold calculated, [µmol/mol]	ISO14687-2 threshold value, [µmol/mol]
NH_3	2	0.9 (2.3*)	0.1
HCl	0.2	0.09	0.05
$C_4Cl_4F_6$	0.2	0.08	0.005

** 2.3 value was obtained using FC voltage recovery after operation in pure H_2. It reflects partial reversibility of NH_3 impact on FC performance.*

- ☐ **The actual threshold for ammonia might be relaxed to 0.5 µmol/mol;**
- ☐ **Existing threshold for total halogenated compounds 0.05 µmol/mol is reasonable.** Need more investigation on the halocarbons decomposition on Pt under PEMFC operating conditions.

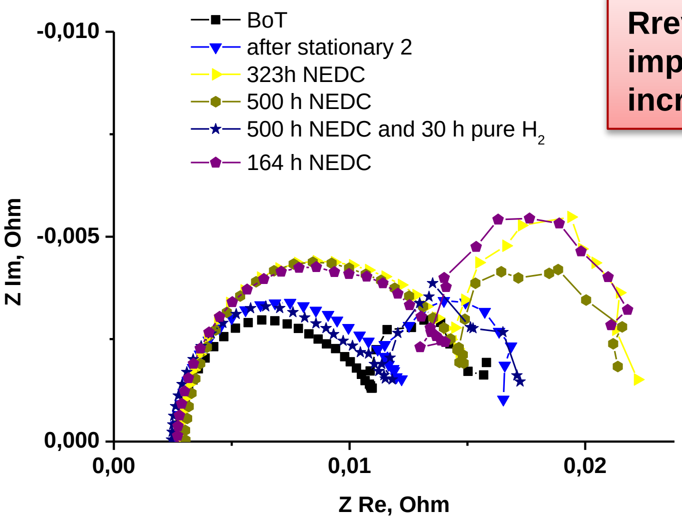
IN-SITU ELECTROCHEMICAL DIAGNOSTICS BY IMPEDANCE SPECTROSCOPY

Reference pure H_2 at 10A



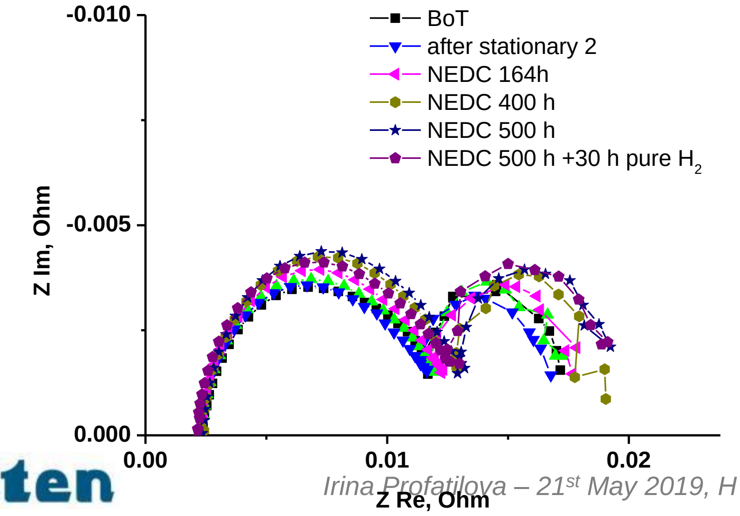
Charge transfer resistance → ORR cathode reaction

2 ppm NH_3 at 10A

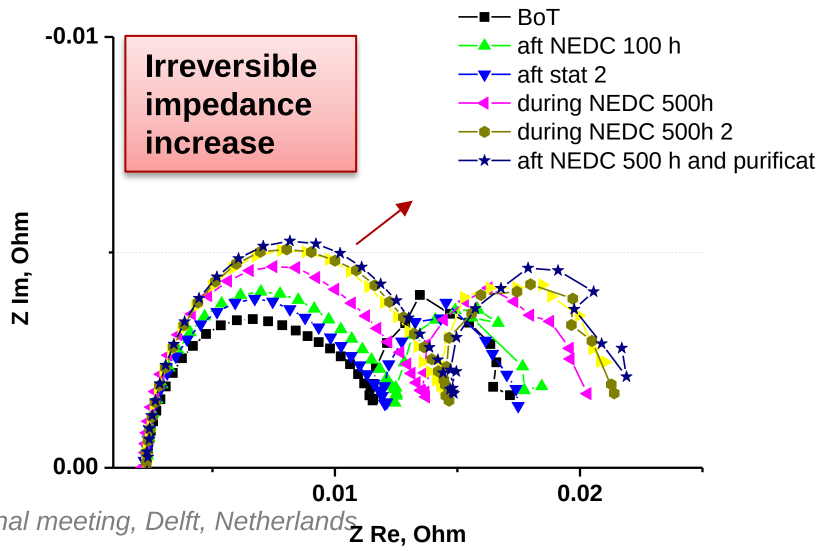


Rreversible impedance increase

0,2 ppm HCl at 10A



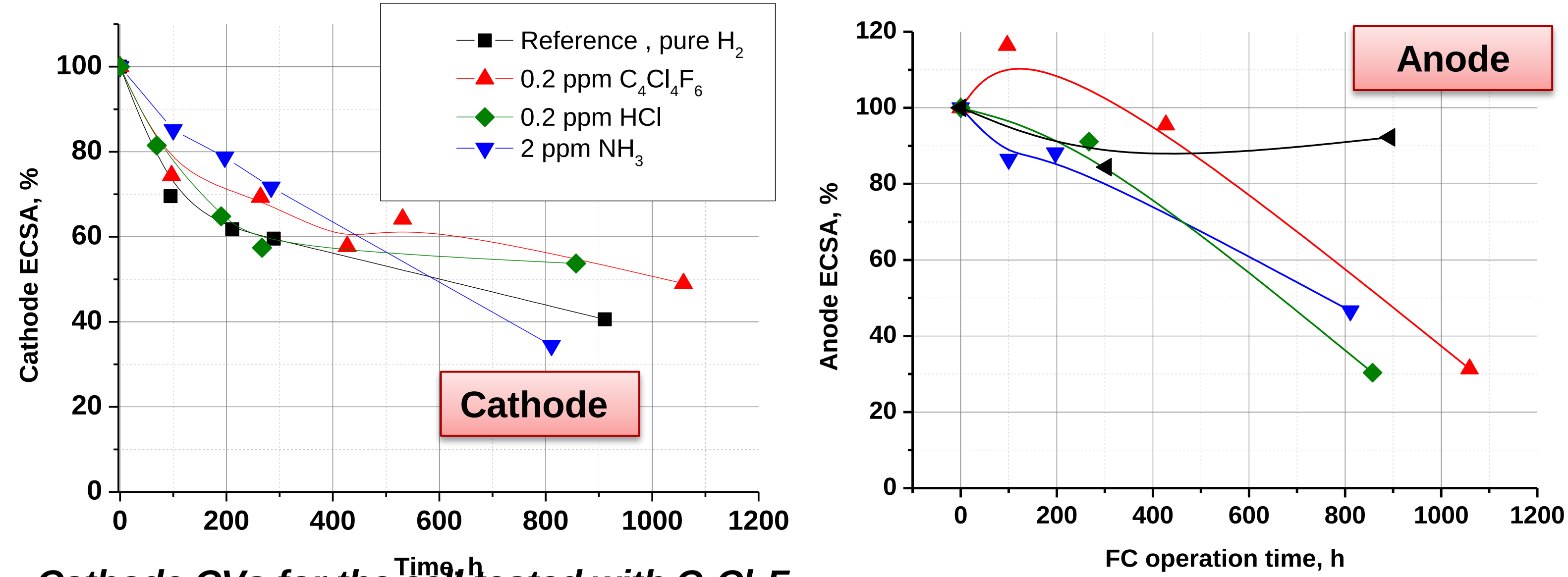
0,2 ppm $C_4Cl_4F_6$ at 10A



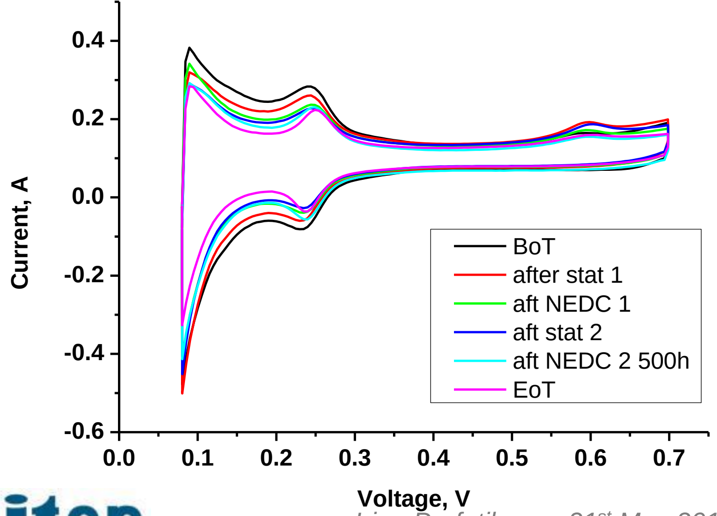
Irreversible impedance increase

IN-SITU ELECTROCHEMICAL DIAGNOSTICS BY CYCLIC VOLTAMMETRY

Relative ECSA decrease between BoT and EoT



Cathode CVs for the cell tested with $C_4Cl_4F_6$



- **Similar cathode ECSA degradation for all cells;**
- **Anode ECSA is more affected by the presence of impurities;**
- **No direct correlation between ECSA for the electrodes and cell degradation rates.**

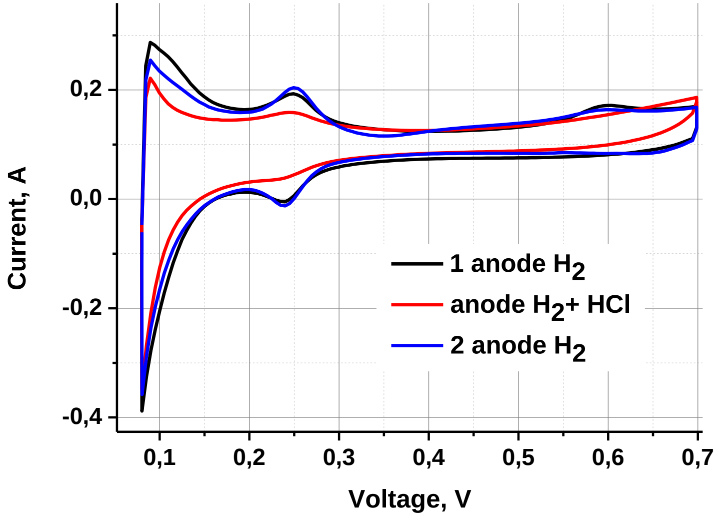
FC POISONING BY HCL: MECHANISM CONSIDERATIONS

- ☐ **Chloride ions adsorption is increasing with electrode potential (0.2 → 0.7 V vs RHE);**
- ☐ **They are responsible for inhibiting the ORR;**
- ☐ **Chloroplatinate ions can be generated electrochemically or chemically:**

$Pt + 6Cl^- \rightarrow PtCl_6^{2-} + 4e^-$, $E^0 = 0{,}742$ V vs SHE

- ☐ **Generated chloroplatinate ions promote growth of Pt particles.**

Cathode CVs taken with H_2 and H_2+HCl supplied on the anode

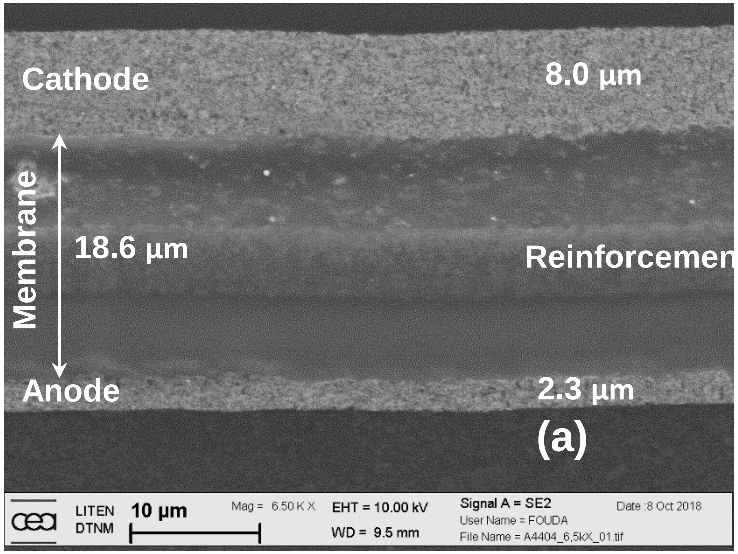


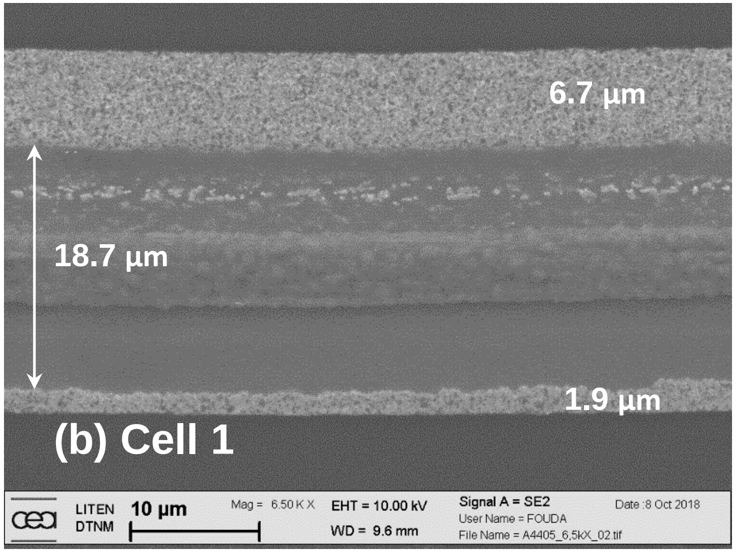
→ Direct reversible impact of HCl on cathode ECSA.

Baturina O. et al, J. Electrochem. Soc., 161 (2014) F365.

SEM MICROSCOPY ANALYSIS

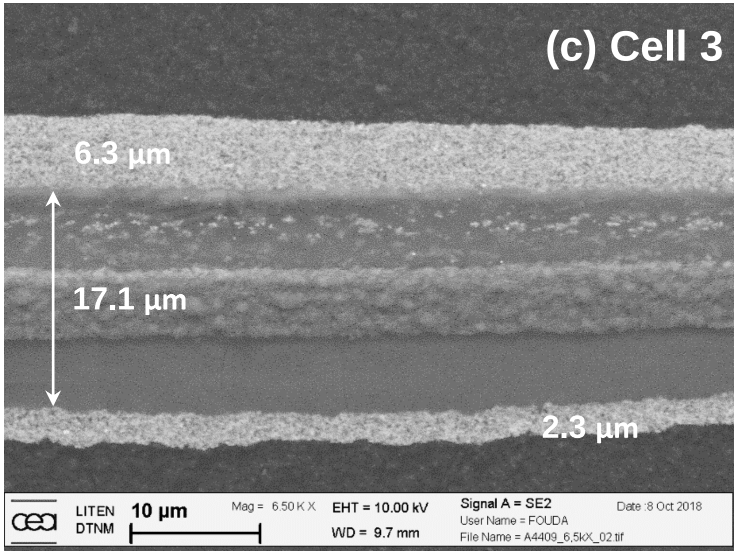
Pristine

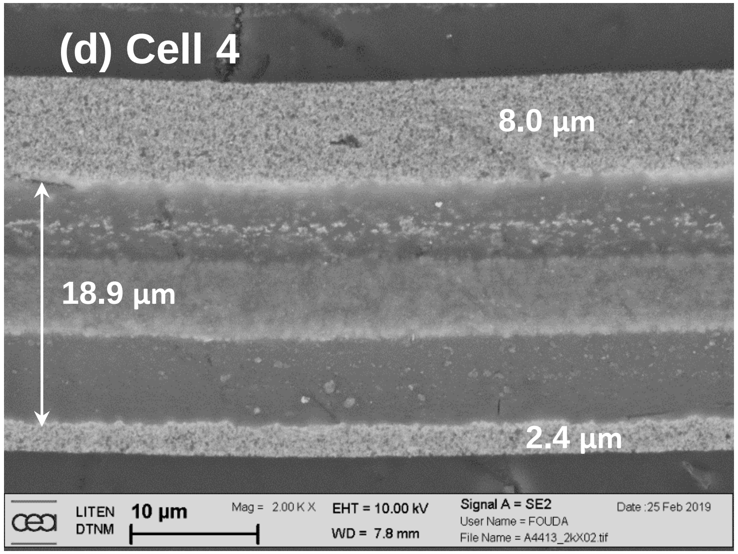




Aged in pure H_2

Aged in $H_2 + NH_3$

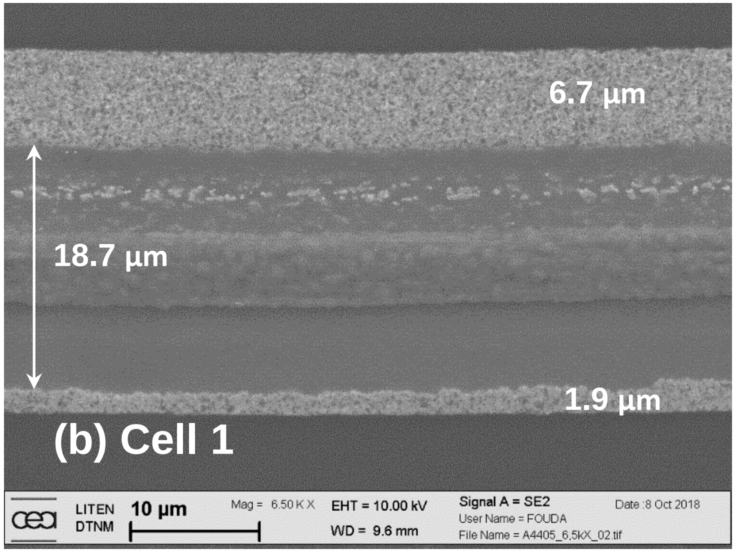


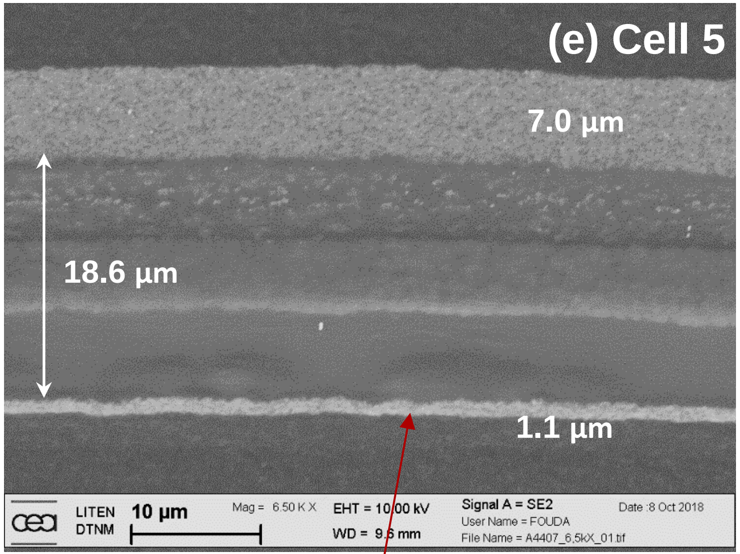


Aged in $H_2 + HCl$

SEM OBSERVATIONS OF MEAs

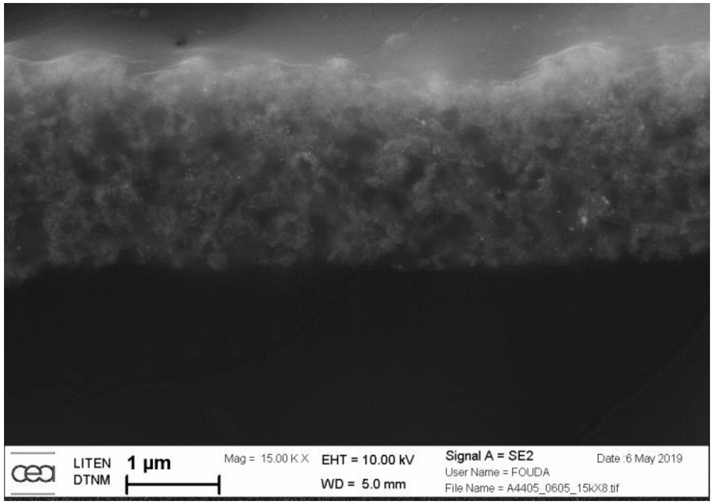
Aged in pure H_2

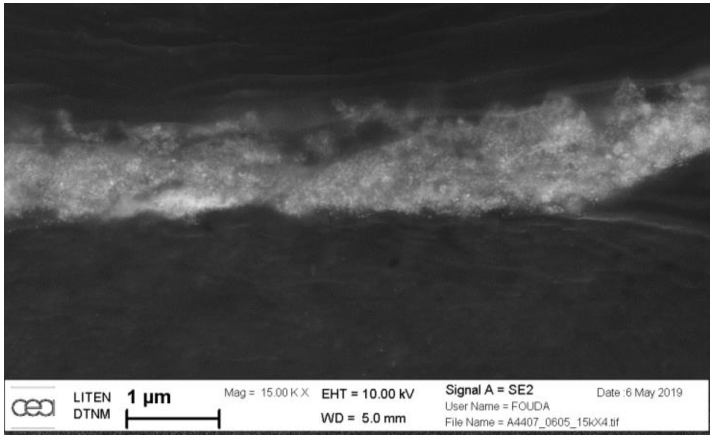




Aged in $H_2 + C_4Cl_4F_6$

Thinner and denser anode active layer

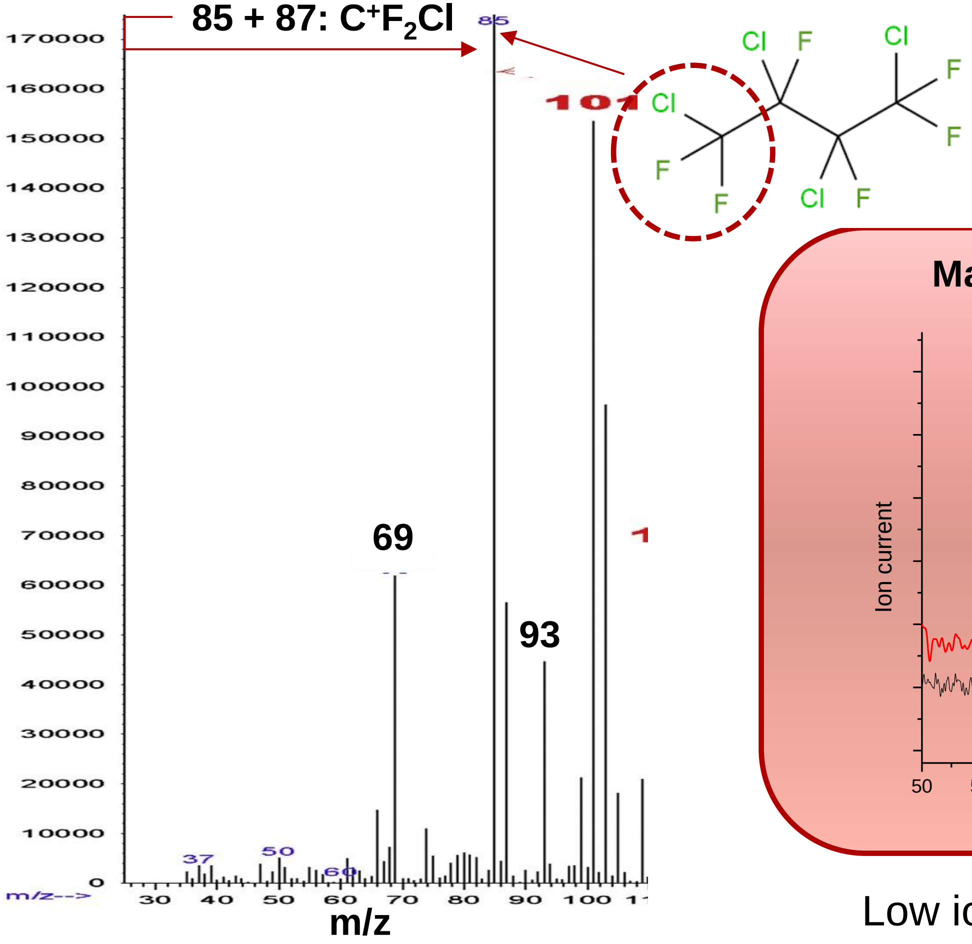




MASS SPECTROMETRY OF $C_4CL_4F_6$

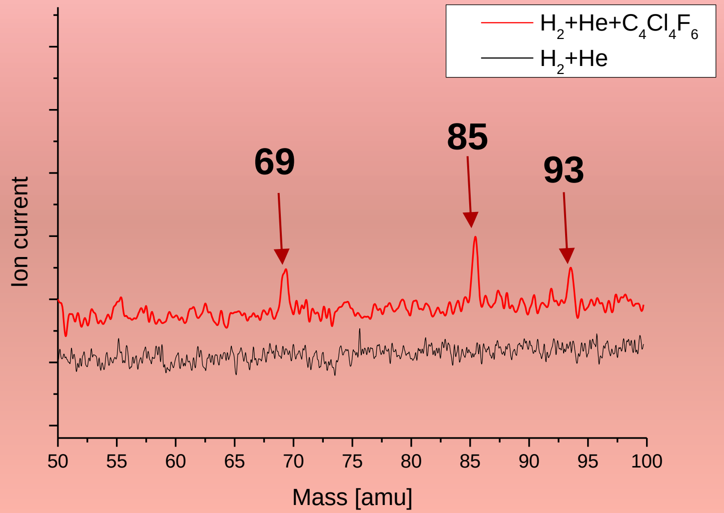
1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane

Mass spectrum of $C_4Cl_4F_6$



Composition of fuel used:
H_2 + 2.7% He + 5.7ppm $C_4Cl_4F_6$

Mass spectra of gas mixtures

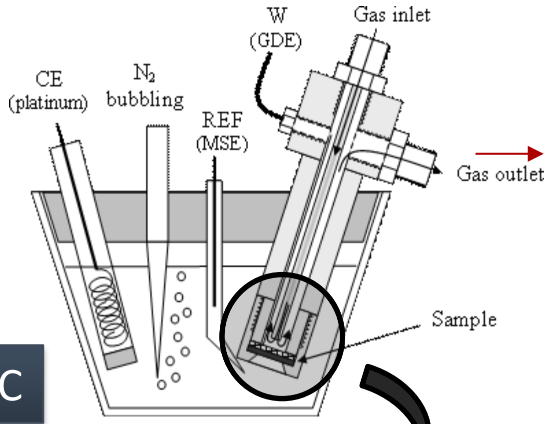


Low ion current due to low content of $C_4Cl_4F_6$ in the gas mixture.

Int. J. Hydrogen Energy 37 (2012) 1770

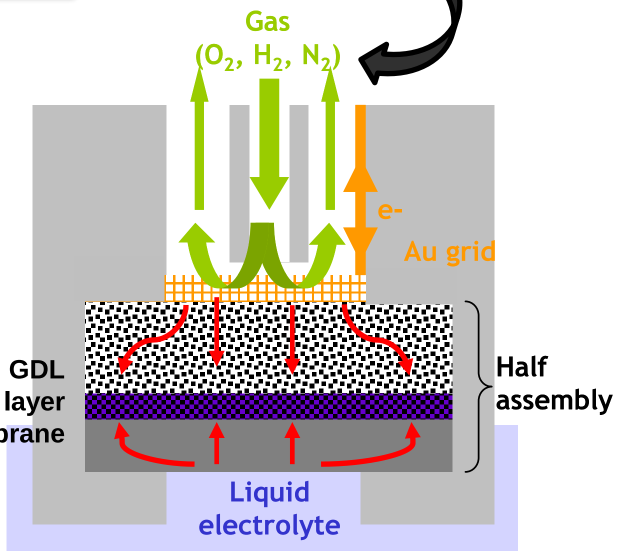
HALF CELL STUDY OF THE IMPACT OF $C_4CL_4F_6$

3-electrode cell with gas-diffusion WE



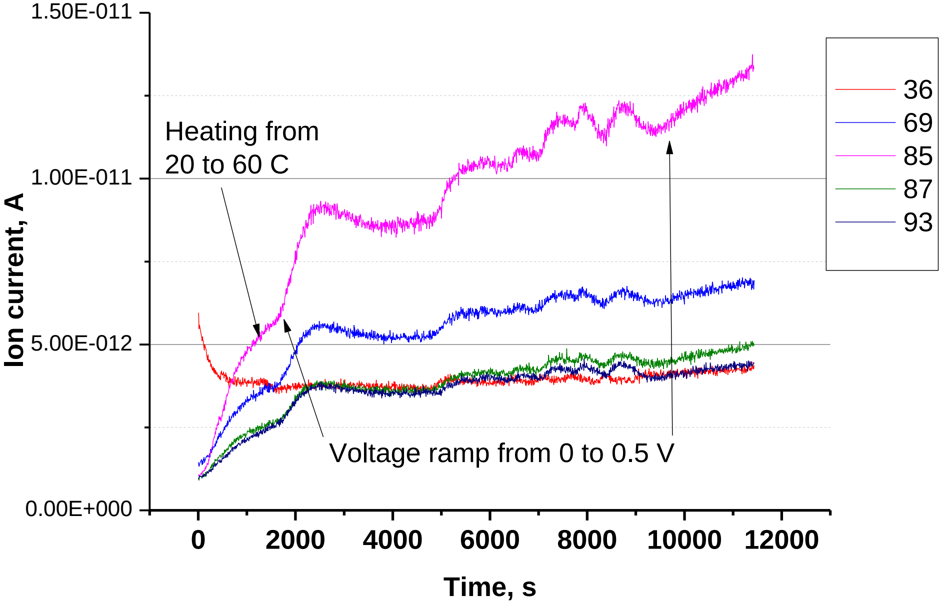
To mass spectrometer GSD 320

60 °C



Half cell assembly

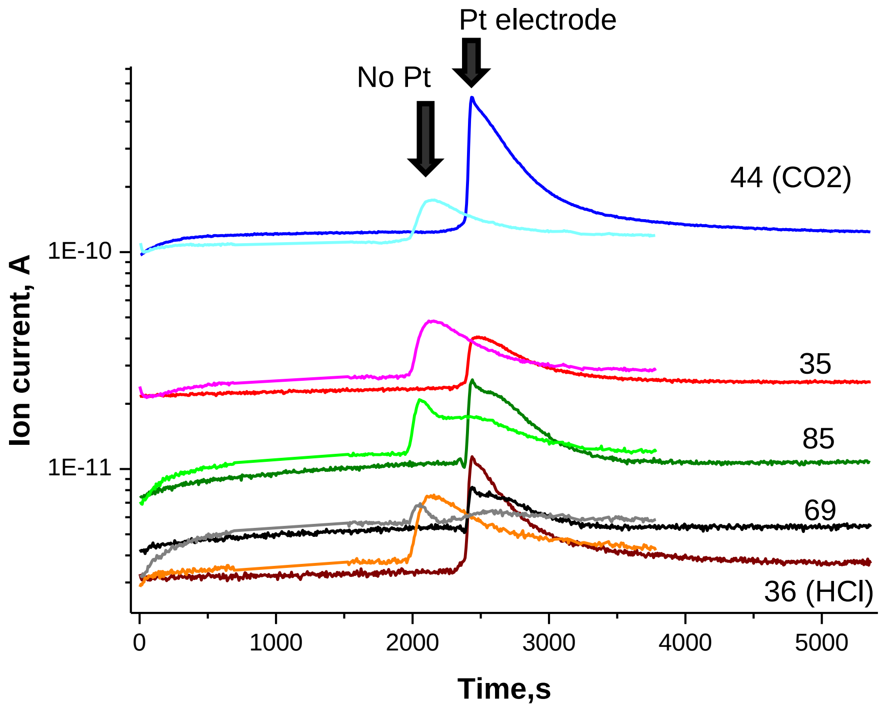
Online MS measurements of Pt based electrode under different fuels



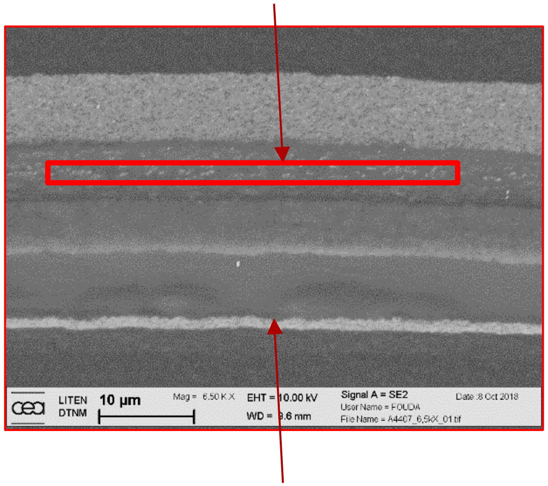
- **Heating and potential increase provoke fragmentation of $C_4Cl_4F_6$ molecule;**
- **High sensitivity to gas bubbles removal from the electrode (introduction of some amount of air is possible).**

HALF CELL STUDY OF THE IMPACT OF $C_4CL_4F_6$

60 °C, 0V vs RHE, H_2 + 5 ppm $C_4Cl_4F_6$ supply either to membrane or to platinum electrode coated onto membrane. Peaks correspond to 1 ml air injection.



Co-existence of O_2, H_2 + $C_4Cl_4F_6$ via crossover and Pt particles in the membrane → oxidative decomposition of halocarbon.



Adsorption and partial reductive decomposition of $C_4Cl_4F_6$ is highly possible.

- **$C_4Cl_4F_6$ reacts with air (O_2) in the MS chamber;**
- **In presence of Pt electrode the proportion of reaction products is changed → indirect evidence of $C_4Cl_4F_6$ decomposition on Pt electrode.**

FC POISONING BY $C_4CL_4F_6$: MECHANISM CONSIDERATIONS

❑ **Halogenated hydrocarbons ($CFCl_3$, CH_3Cl, CH_2Cl_2, CCl_4, CH_3-CCl_3, etc.) behavior on Pt electrode at low T includes:**

- Adsorbtion on Pt at low potentials ~0.2 V vs RHE
- Partial reductive desorption/dehalogenation with the formation of saturated alkanes
- Oxidative decomposition with a formation of HCl and CO_2 (>0.5 V vs RHE).

U. Muller et al. Electrochim. Acta 42 (1997) p. 2499; K.C. McGee et al., J. Electrocatal., 157 (1995) p. 730; B. Bansch et al., Electrochim. Acta, 33 (1988) p. 1479; H. Baltruschat et al., Electrochim. Acta, 38 (1993) p. 281.

❑ **According to our data, $C_4Cl_4F_6$ behavior in fuel cell includes:**

- Adsorption at low potentials is likely
- Overpotential creation for HOR and carbon corrosion
- Crossover to cathode side, HCl formation and increase in cathode charge transfer resistance via Cl^- adsorption
- Pt dissolution and electrode thinning.

CONCLUSIONS

- **The negative impact of trace concentration of NH_3, HCl and $C_4Cl_4F_6$ on a long term performance od PEMFC under mixed stationary and dynamic protocol was investigated and quantified;**

- **NH_3, HCl and $C_4Cl_4F_6$ provoke irreversible performance losses of ~17-37 µV/h at 0.6 A/cm^2 after 900h of the test (not acceptable);**

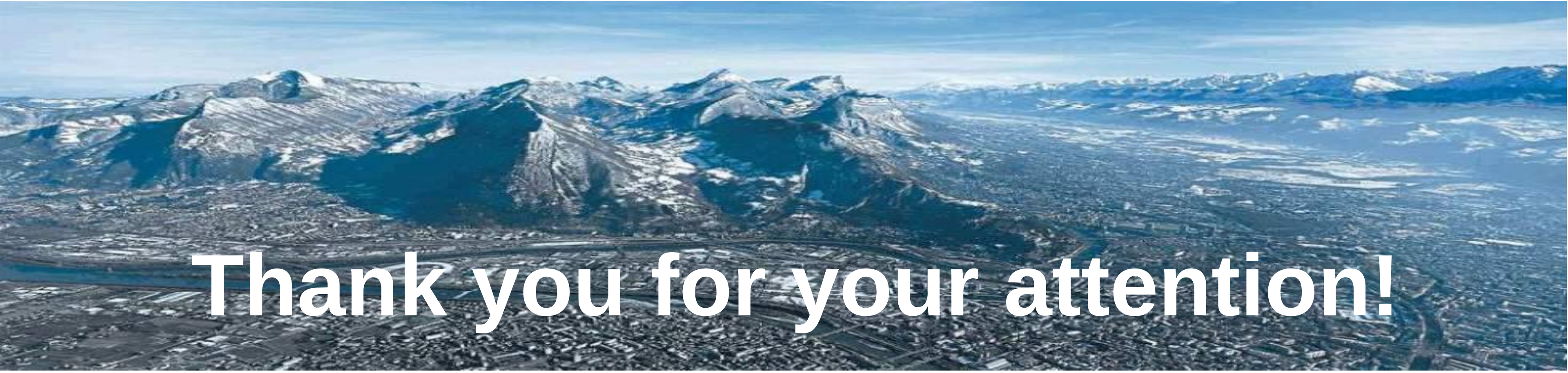
- **$C_4Cl_4F_6$ exposure resulted in the highest reversible and irrecoverable FC performance losses;**

- **The existing value for acceptable NH_3 concentration can be relaxed based on the results obtained while that one for halogenated compounds seems to be consistent;**

- **SEM and online MS investigation showed possibility of $C_4Cl_4F_6$ decomposition on Pt electrode leading to the active layer thinning and performance failure;**

- **More study on the behavior of organic halogenated compounds under FC conditions is necessary.**

ACKNOWLEDGEMENTS



Thank you for your attention!

The research leading to these results has received funding from the in-progress Joint Research Project « Metrology for sustainable hydrogen energy applications » supported by the European Metrology Programme for Innovation and Research (EMPIR). The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States.

Irina.profatilova@cea.fr

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States