DE LA RECHERCHE À L'INDUSTRIE

Impact of key impurities on fuel cell degradation

Irina Profatilova[1], Marie Heitzmann[1], Pierre-André Jacques[1], Andrés Rojo Esteban[2], Thomas Bacquart[3]

[1]Atomic Energy and Alternative Energies Commission (CEA), LITEN, Grenoble, France

[2]CEM Spanish Metrology Center, Madrid, Spain

[3]National Physical Laboratory, Teddington, UK

INTERNATIONAL WORKSHOP

Metrology for sustainable hydrogen energy applications

7-8th November, 2018

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MOTIVATION

Present requirements for H_2 quality:

Impurity in H_2	ISO14687-2 threshold value, [µmol/mol]
NH_3	0.1
HCl	0.05
$C_4Cl_4F_6$	0.005*

Not found in H_2 samples from SMR, PEM water electrolysis and chlor-alkali membrane electrolysis within the HYDROGEN project

→ High cost of H_2 purification

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

→ NH_3 can present in fuel reformate from different processes in case of not enough/failure of purification;
→ Metal hydride catalyzed formation of NH_3 from N_2 and H_2;
→ Ambient air impurities can contaminate operating FC;
→ $C_4Cl_4F_6$ was found in H_2 from HRSs (*HyCora project results; Int. J. Hydrogen Energy 37 (2012) 1770*).

The impact of NH_3, HCl and $C_4Cl_4F_6$ in trace concentrations on FC performance is poorly investigated especially over long term and under driving cycling conditions.

OBJECTIVES OF THE WORK

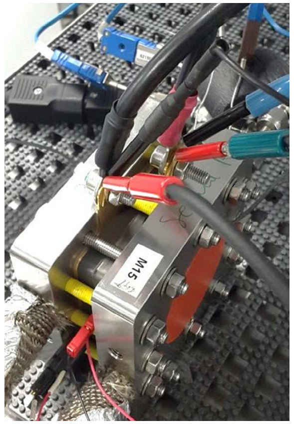
- Understand the impact of low concentrations of NH_3, HCl, $C_4Cl_4F_6$ in fuel on PEM FC performance under dynamic automotive load cycling;

- Focus on short- and long-term performance and reversibility of contamination effects;

- Provide recommendations on the acceptable NH_3, HCl and $C_4Cl_4F_6$ concentration in H_2 for the automotive application.

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;
- Bubbler bypass for the impurities.

MEA characteristics	
Anode Pt loading, mg/cm^2	**0.11-0.13**
Cathode Pt loading, mg/cm^2	**0.34**
Membrane	**Gore 18μm**
Fuel used	**H_2 pure (99.995%) 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
ANODE	Fuel gas inlet humidity	RH.Si.A DPT.Si.A	% RH °C	50 64 @80°C
ANODE	Fuel gas inlet pressure (absolute)	p.Si.A	kPa	250
ANODE	Fuel gas composition	Conc.Si.A.H2, Conc.Si.A.GasX		According to H_2 5.0 quality
ANODE	Fuel stoichiometry	Stoic.Si.A	-	1.3
CATHODE	Oxidant gas inlet temperature	T.Si.C	°C	85
CATHODE	Oxidant gas inlet humidity	RH.Si.C DPT.Si.C	% RH °C	30 53 @80°C
CATHODE	Oxidant gas inlet pressure (absolute)	p.Si.C	kPa	230
CATHODE	Oxidant	Conc.Si.C.O2, Conc.Si.C.GasX	-	According to ISO 8573-1:2010
CATHODE	Air stoichiometry	Stoic.Si.C	-	1.5
CATHODE	Minimum current density for stoichiometry operation	I.S.MinGasFlow	A/cm^2	0.2

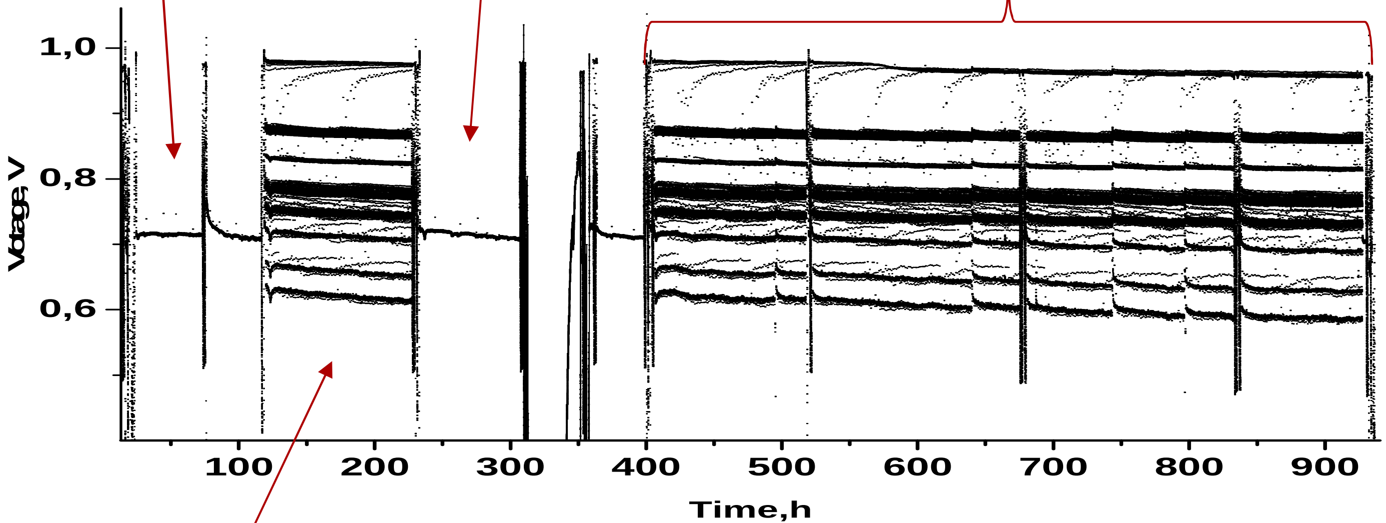
doi:10.2790/54653

EXAMPLE OF VOLTAGE PROFILE FOR REFERENCE TEST

Stationary test 1 @ 0.6 A/cm² for 48 h + electrochemical characterization

Stationary test 2 @ 0.6 A/cm² for 72 h + electrochemical characterization

NEDC cycling test for 500 h + electrochemical characterization



NEDC cycling test for 100 h + electrochemical characterization

Electrochemical characterization and purification protocol:

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

Details of New European Driving Cycle (NEDC) protocol

NEDC: dynamic load with I max = 1 A/cm² and I min = 0.2 A/cm² (1180 s).

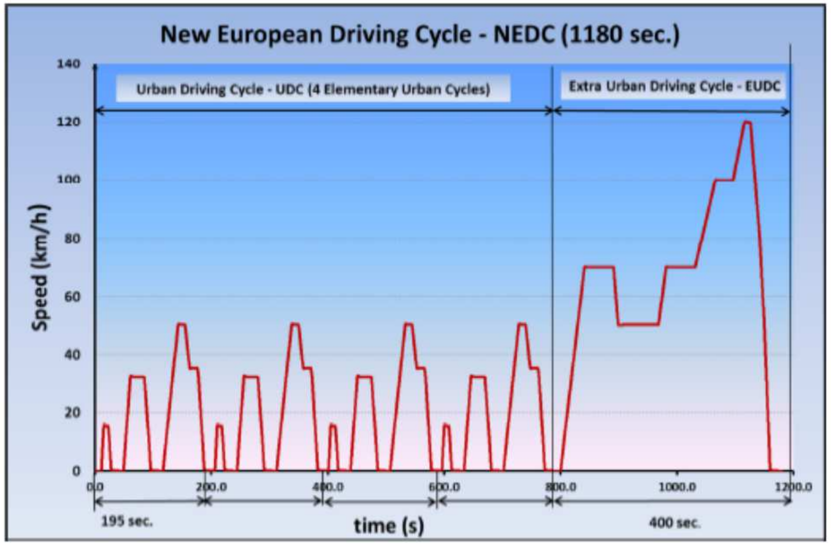


Figure 4:

NEDC profile according to EU Directive 98/69/CE

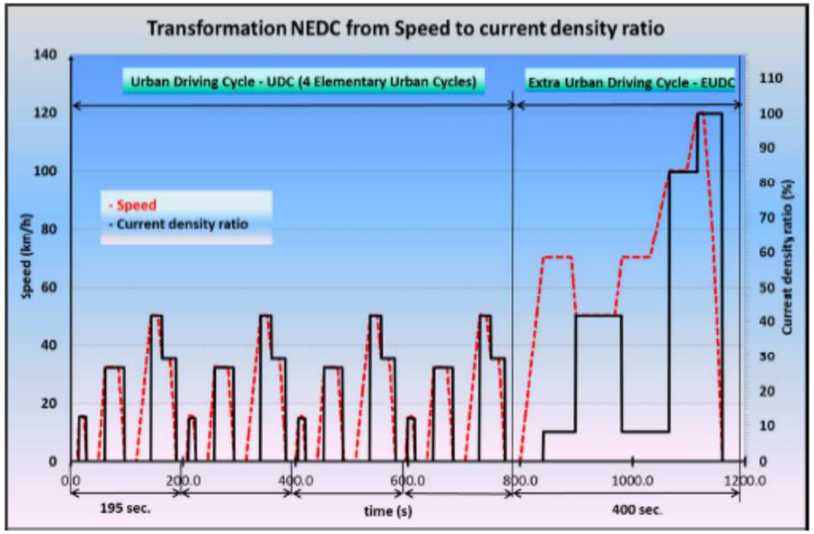


Figure 6:

Profile of ratio of current density to maximum current density expressed as percentage vs cycle duration adapted for testing PEMFC single cells to resemble the NEDC cycle (vehicle speed vs. cycle duration) as a load (current) profile

EU Harmonised Test Protocols for PEMFC-MEA Testing in Single Cell Configuration for Automotive Applications

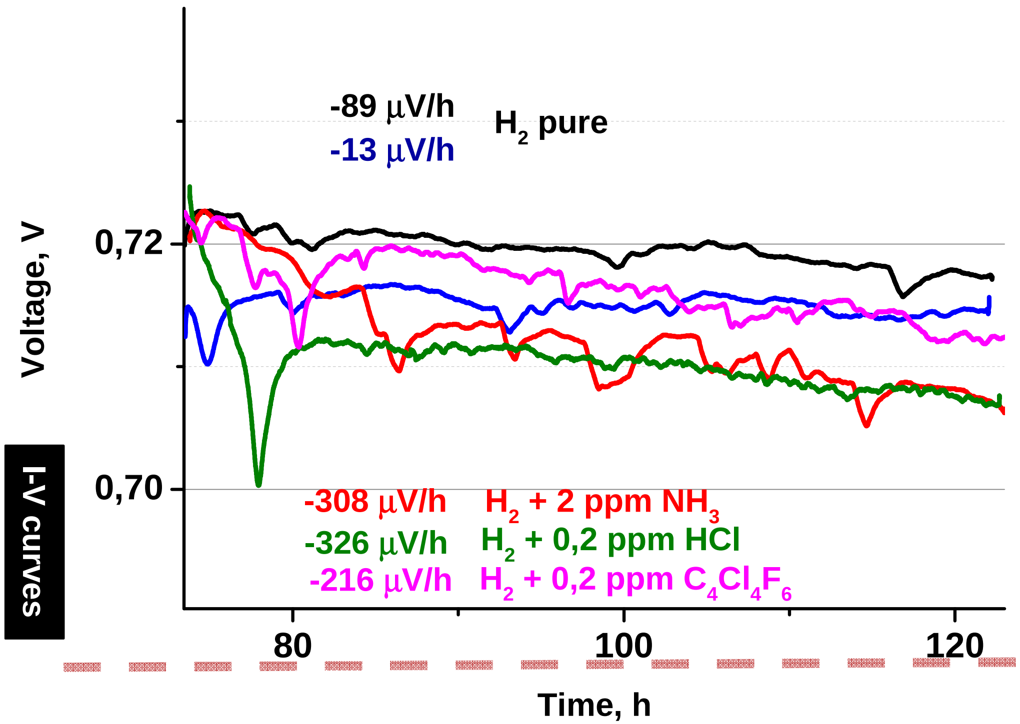
Electrochemical tests for the FCs with and w/o pollutants:

experimental data

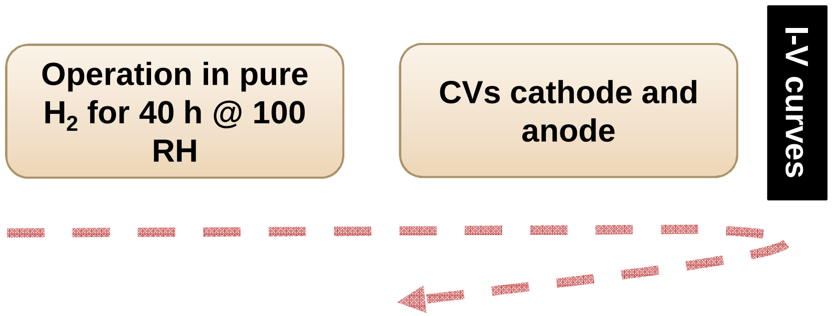
STATIONARY 1 TEST

Hydrogen

0.6 A/cm² voltage ageing profiles



- Degradation rates correspond to **reversible + irreversible losses;**
- **More degradation in presence of impurities;**
- Irreversible degradation was quantified by pol. curves after cleaning with pure H_2 (40 h at 100% RH) and CVs**.**



Non-recoverable degradation rate estimation

	Reference	2 ppm NH_3	0,2 ppm HCl	0,2 ppm $C_4Cl_4F_6$
Irrevers. degradation rate @ 0.6A/cm², µV/h	0	0	-60	0

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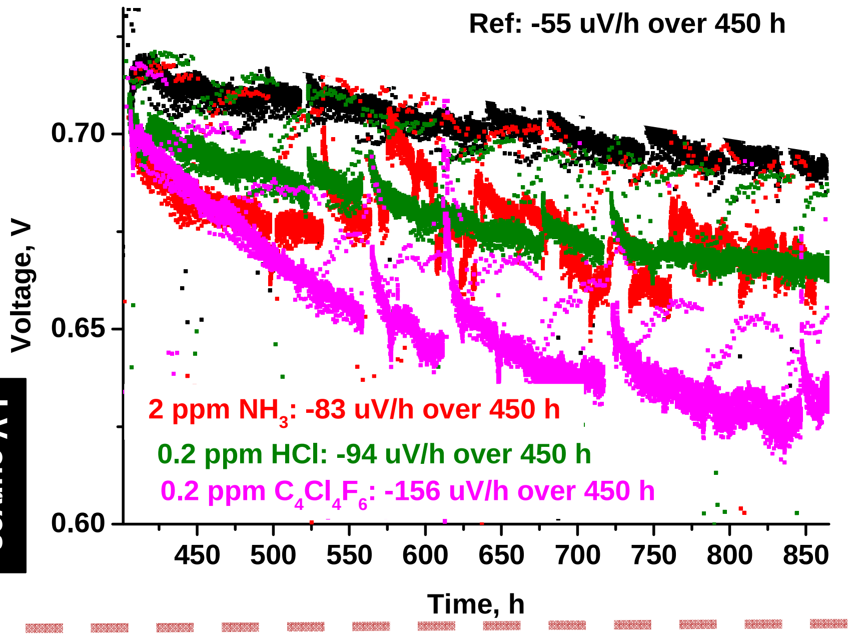
Extracted at 0.6 A/cm^2 from NEDC profile

I-V curves



- **The lowest total degradation rate for the cell operated in pure H_2;**
- Instability of performance for the cell under $H_2 + NH_3$.

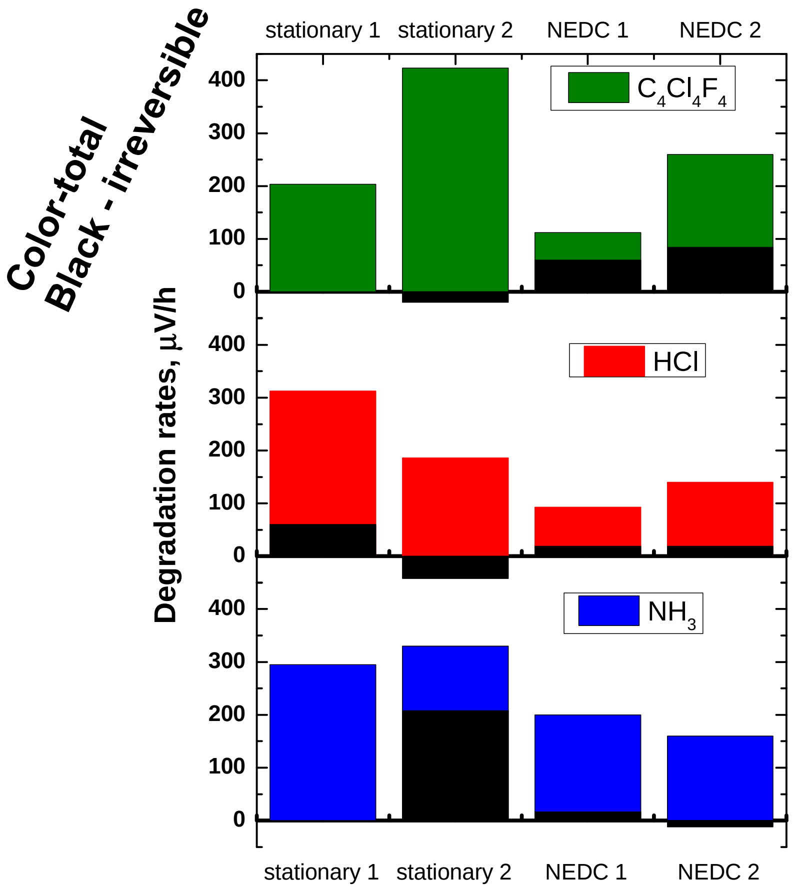
I-V curves → CVs cathode and anode → 36 h in pure H_2 → I-V curves

Non-recoverable degradation rate estimation

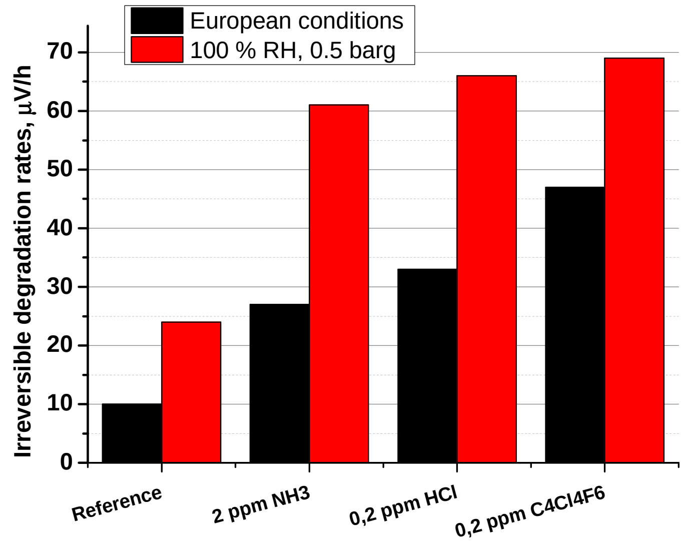
	Reference	2 ppm NH_3	0,2 ppm HCl	0,2 ppm $C_4Cl_4F_6$
Irrevers. degradation rate @ 0.6 A/cm^2, µV/h	-19	-7	-38	-103

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 /cm^2



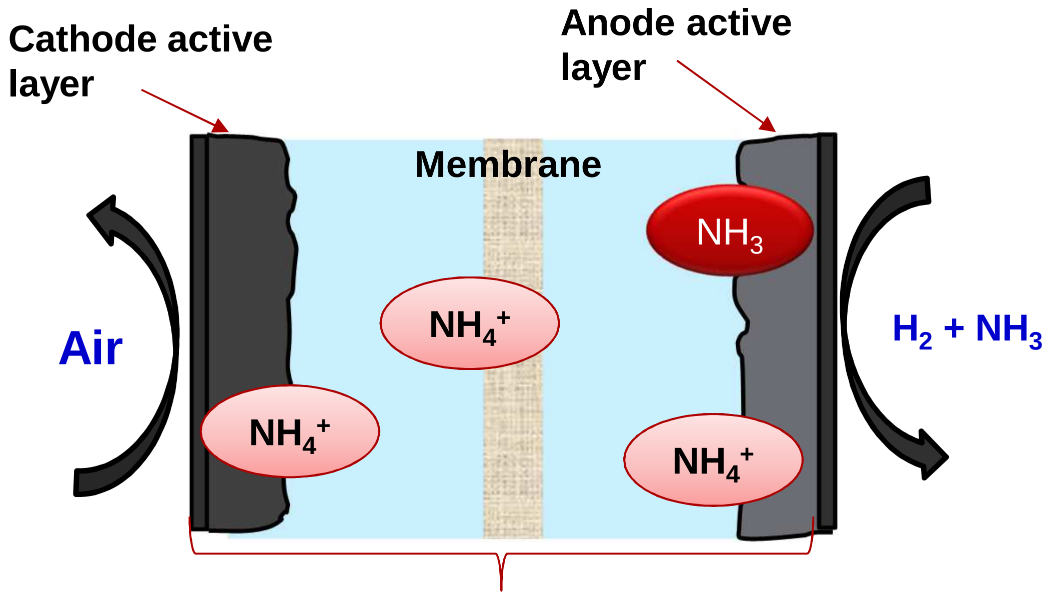
- **Less impact** of contaminants on FC under **dynamic load** compared to stationary operation**;**
- **Short-term (~50h) exposure to 2 ppm NH_3 and 0.2 ppm $C_4Cl_4F_6$ was completely reversible;**
- **The largest part of performance losses is recoverable.**

EFFICIENCY OF CLEANING TECHNIQUES

Technique	Impact on FC performance
2- 3 polarisation curves	Efficient only for PtO_x removal
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 recovery, efficient for NH_3 removal.

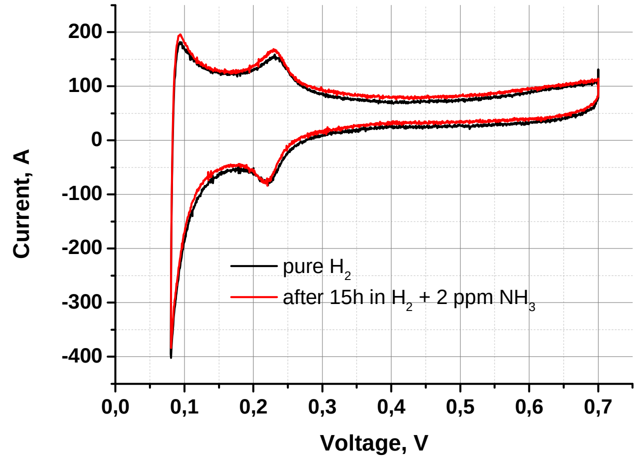
Electrochemical characterization and possible mechanisms for FC poisoning

FC POISONING BY NH_3: MECHANISM CONSIDERATIONS



NH_3 + Nafion-H^+ → Nafion-NH_4^+

Anode CVs before and after contamination by NH_3 (EoT curves)



No direct impact of NH_3 on anode ECSA

Decrease in proton conductivity and water uptake:

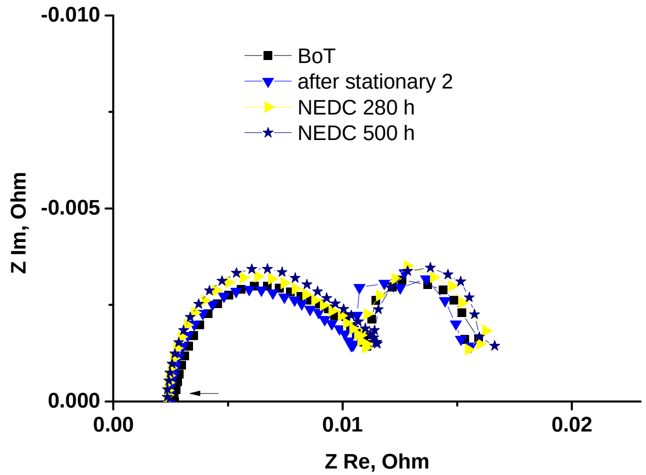
- in the membrane
- in the active layers.

Impact on ORR and HOR:

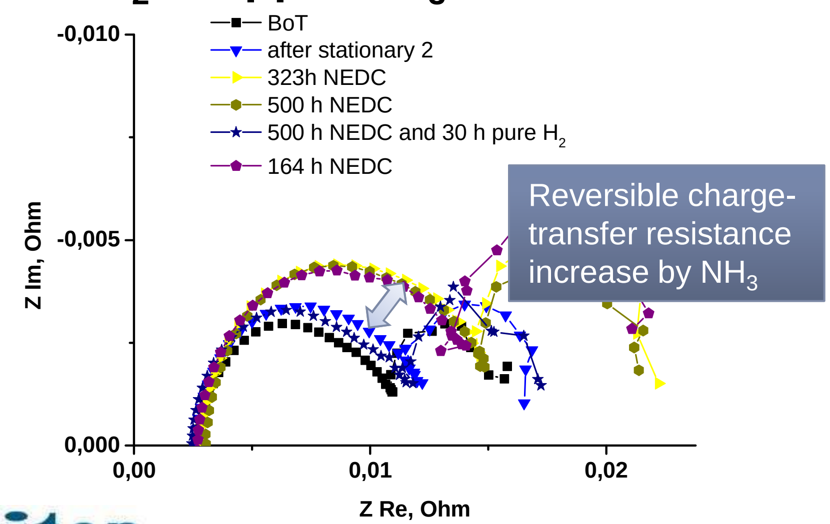
- via adsorption on catalyst surface
- via loss of a contact between the catalyst and the ionomer.

Halseid R et al, J. Electrochem. Soc., 151 (2004) A381; Uribe F.A. et al., J. Electrochem. Soc., 149 (2002) A 293; Gomez Y.A., J. Electrochem. Soc., 165 (2018) F 189.

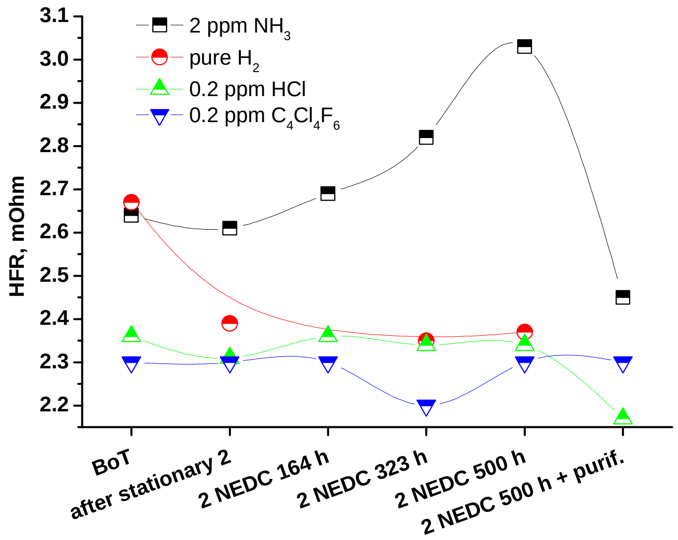
Reference pure H_2 at 10A



H_2 + 2 ppm NH_3 at 10 A



High frequency resistance variation



→ Elevated membrane resistance by NH_3

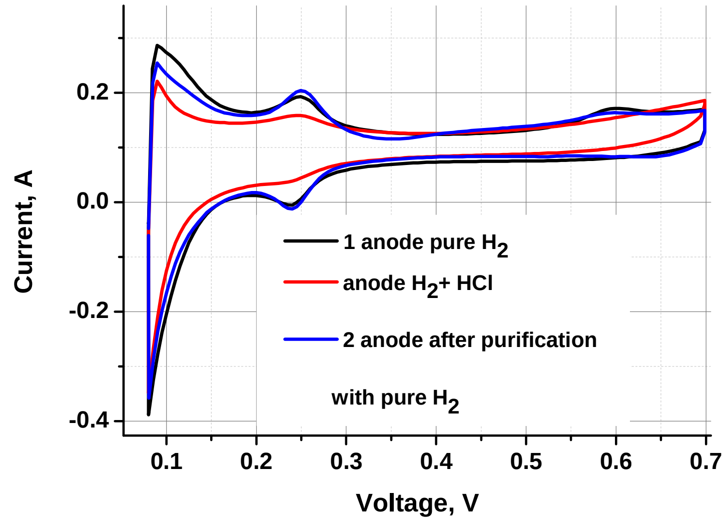
FC POISONING BY HCl AND $C_4Cl_4F_6$: MECHANISM CONSIDERATIONS

- Chloride ions are responsible for inhibiting the ORR via adsorption;
- 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 the growth of Pt particles.
- H_2O_2 generation is possible with further membrane degradation;
- There is no literature data on the impact of $C_4Cl_4F_6$;
- $C_4Cl_4F_6$ can be adsorbed on Pt surface and partially decomposed with the formation of HCl and HF in FC test conditions.

Cathode CVs taken with H_2 and H_2+HCl supplied on the anode (EoT curves)

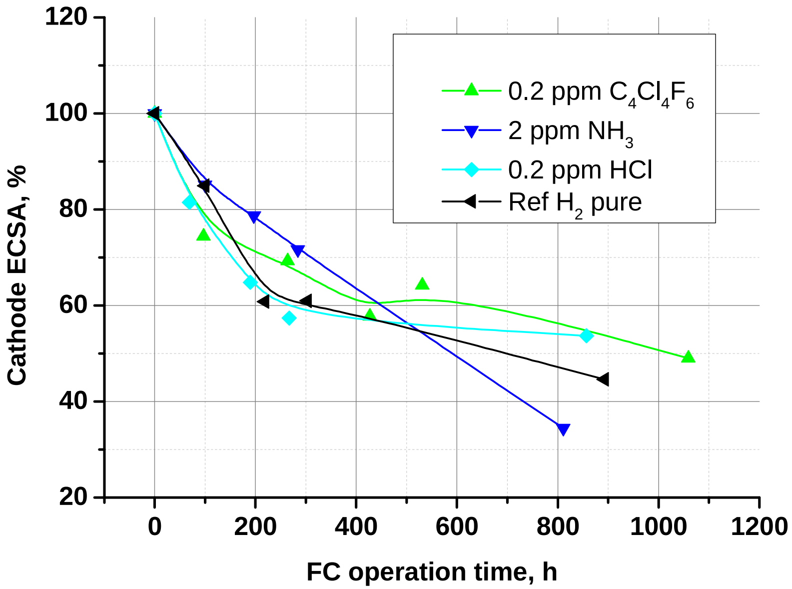


→ Direct reversible impact of HCl on cathode ECSA.

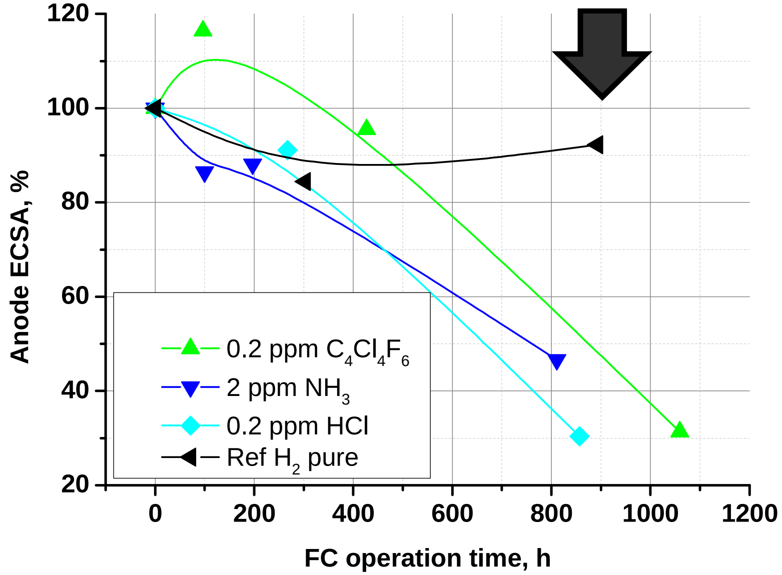
Baturina O et al, J. Electrochem. Soc., 161 (2014) F365.

CHANGES IN ELECTRODE ACTIVE SURFACE IN PRESENCE OF IMPURITIES

Cathode catalyst ECSA



Anode catalyst ECSA

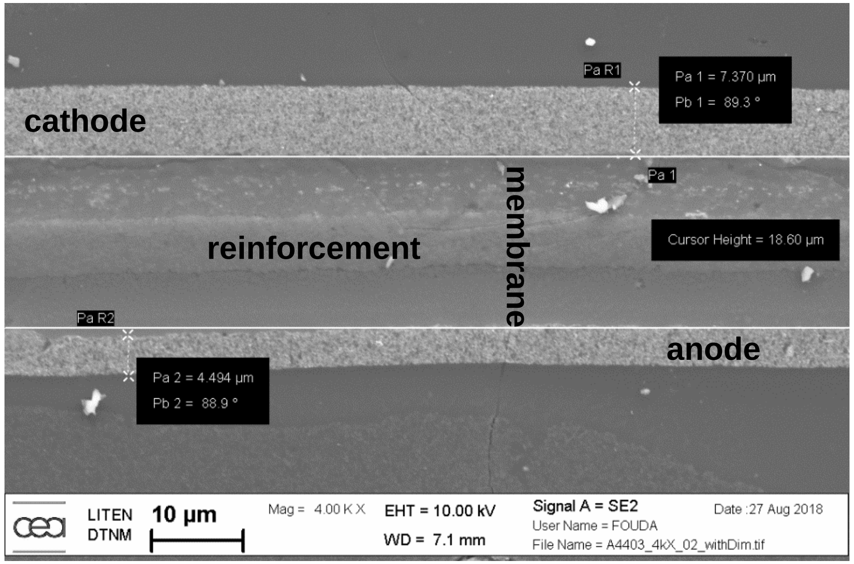


→ Very important cathode ECSA drop with and without the contaminants.

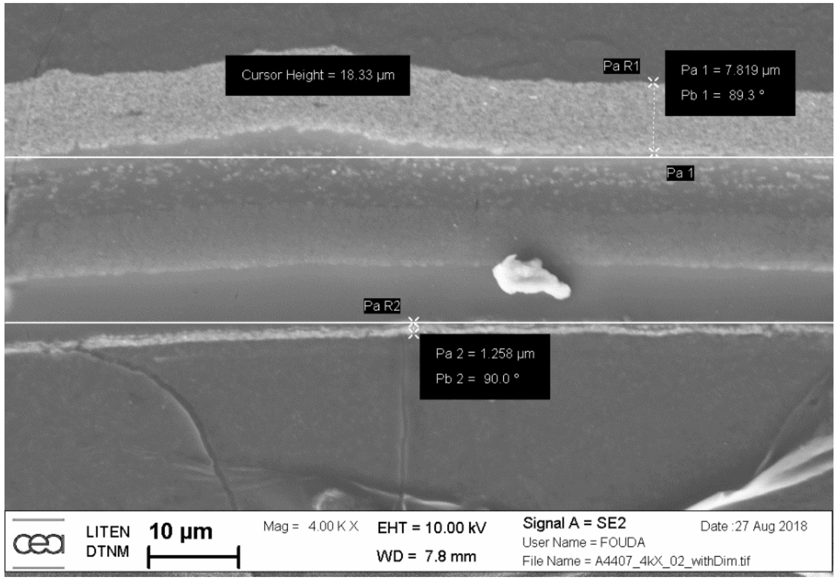
→ Loss of anode ECSA only in presence of impurities in H_2.

PRELIMINARY CROSS-SECTION SEM OBSERVATIONS RESULTS

Reference MEA tested in pure H_2 for 900 h



MEA tested in H_2 + 0.2ppm $C_4Cl_4F_6$



- Striking difference in anode active layer thickness after the durability tests;
- Anode tested with $C_4Cl_4F_6$ impurity is 3 times thinner (possible Pt complexation by HCl and washing-off/re-deposition in the membrane).

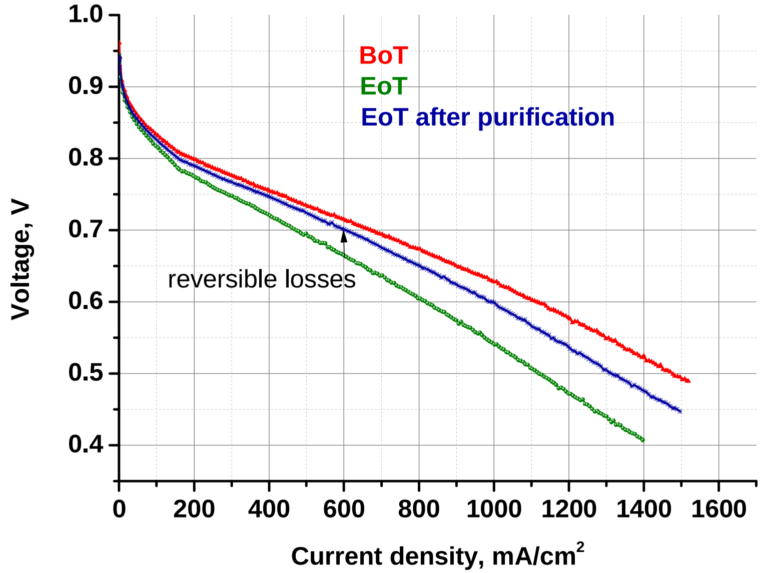
Calculations of acceptable impurities concentrations in H_2

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.

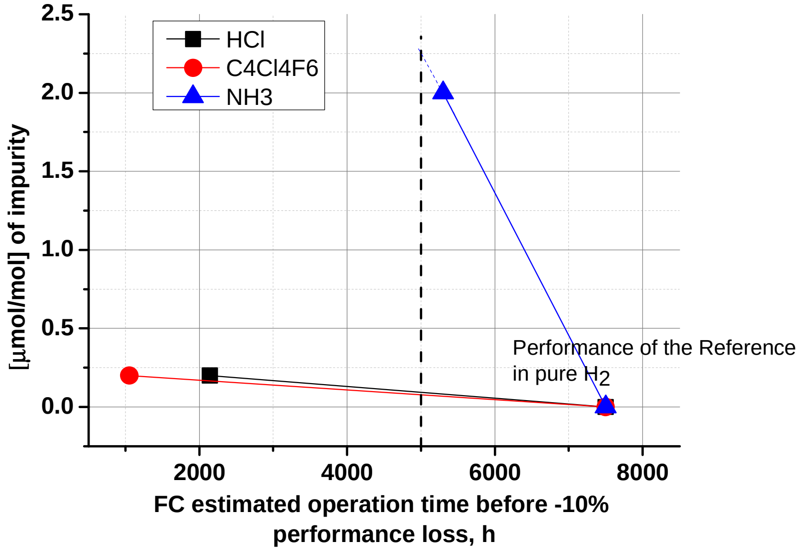
Example of polarization curves for H_2 + 2 ppm NH_3



-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.

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.** However, it makes sense to refer it to real molar concentration of the impurity and not to atom of halogen.

CONCLUSIONS

- The negative impact of trace concentration of NH_3 (2 ppm) and HCl (0.2 ppm) in fuel **is less important** for the PEMFC **in case of dynamic load** compared to stationary operation;

- Full performance recuperation is possible after a short term NH_3 and $C_4Cl_4F_6$ injections (~50 h).

- However, **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);

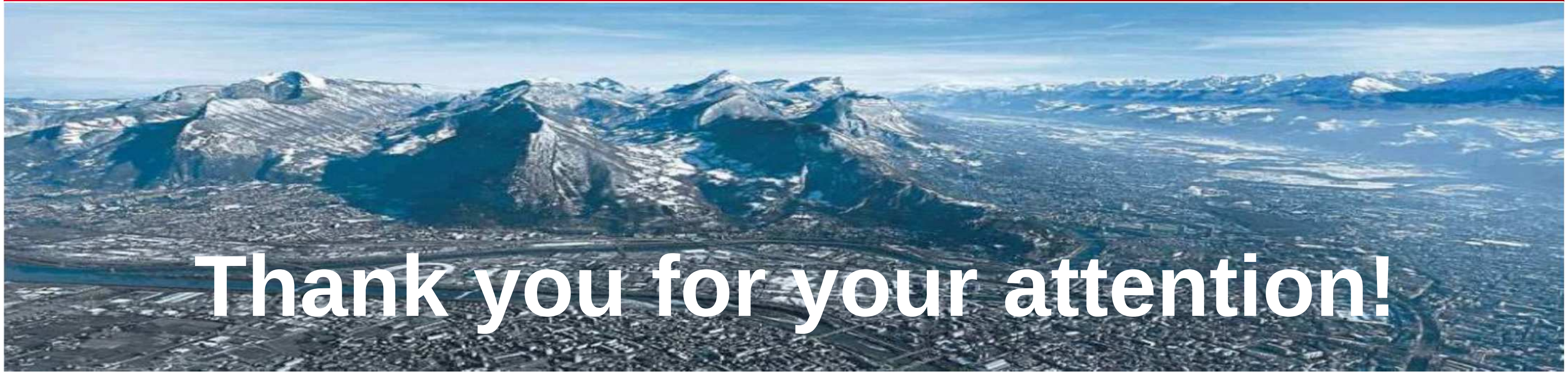
- Cell operation in pure H_2 at high RH is an efficient performance recovery strategy after the cell contamination with NH_3;

- **The actual threshold for ammonia can be relaxed to 0.5 µmol/mol** while that one for halogenated compounds is reasonable.

PROSPECTIVE

- **Investigation of linearity of the impact of impurities on a fuel cell performance under dynamic load can increase the precision of a calculated thresholds.**
- **The mechanism of FC poisoning by $C_4Cl_4F_6$ and other organohalogenates requires further investigation** since this is real impurity, which was found in HRS samples, but it not investigated before.
- **Publication in peer-review journal is planned.**

ACKNOWLEDGEMENTS



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

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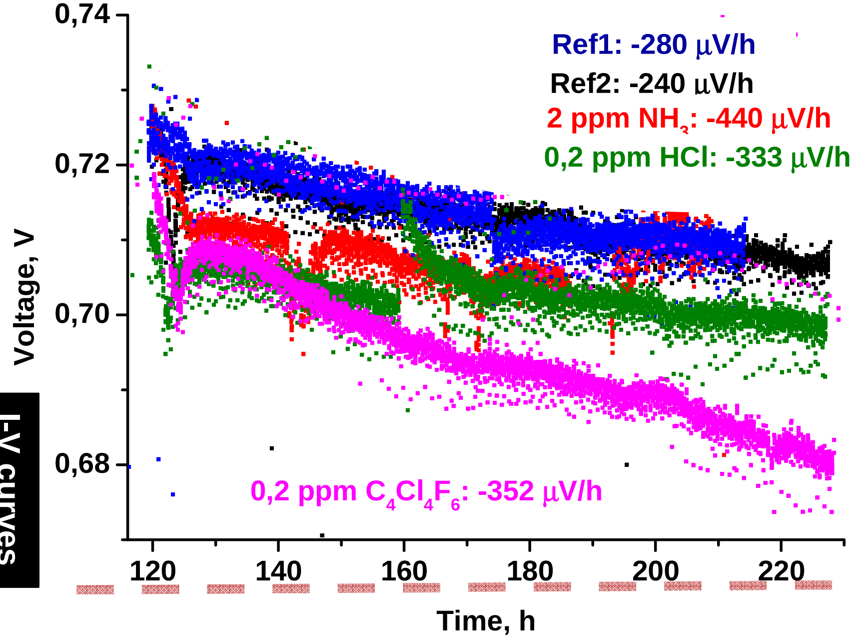
NEDC CYCLING 100 H

Data extracted at 0.6 A/cm² from NEDC profile



- **Elevated total degradation rates in presence of impurities;**
- Cleaning was performed only using CVs → can be not enough;
- **Irreversible performance losses taken from pol. curves are higher for contaminated H_2.**

CVs cathode and anode

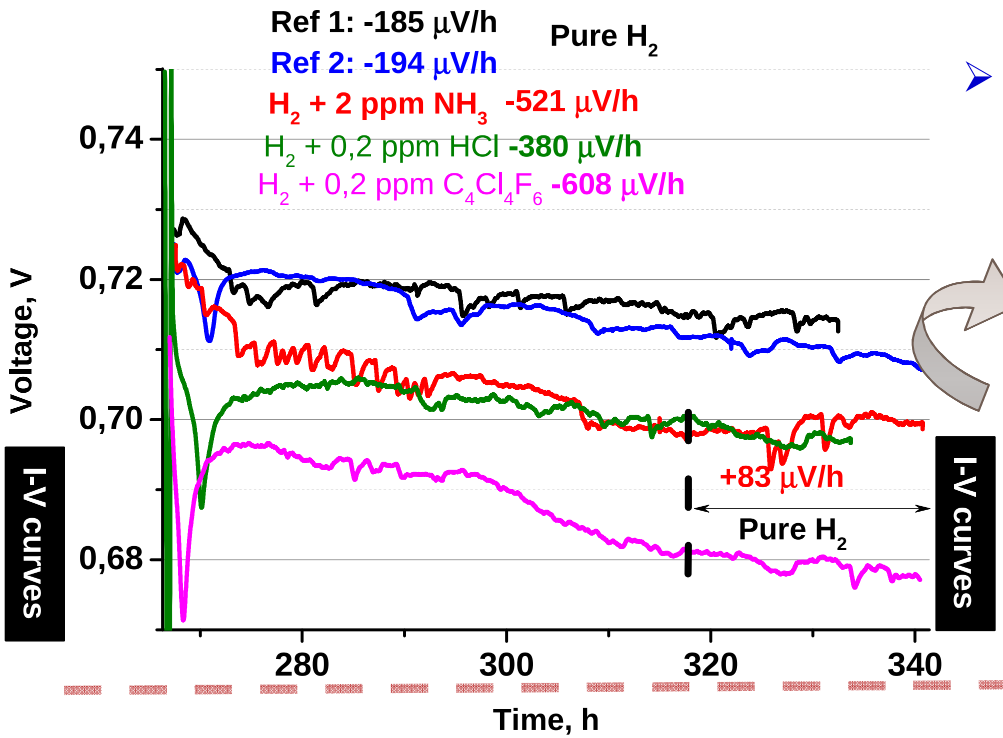
I-V curves

Non-recoverable* degradation rate estimation

	Reference	2 ppm NH_3	0,2 ppm HCl	0,2 ppm $C_4Cl_4F_6$
Irrevers*. degradation rate @ 0.6A/cm², µV/h	-26	-42	-45	-86

STATIONARY 2 TEST

0.6 A/cm² voltage ageing profile



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

0	-274	-164	-95 (3rd) µV/h
Ref	NH_3	HCl	$C_4Cl_4F_6$

6h pure H_2 100 RH → CVs cathode and anode → I-V curves

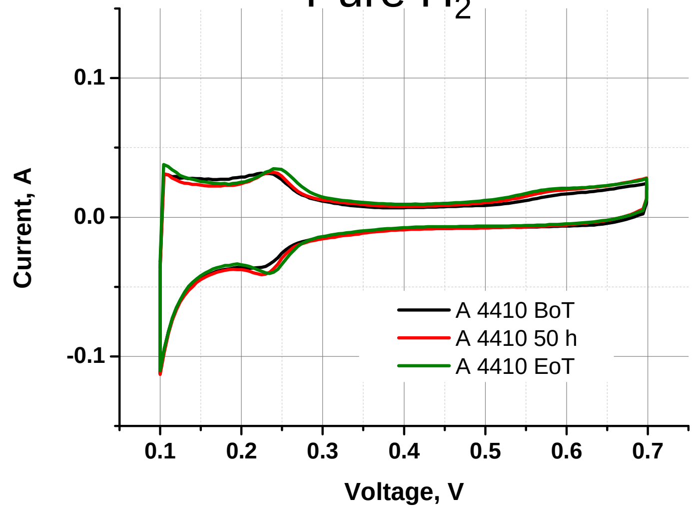
Non-recoverable degradation rate estimation

	Reference	2 ppm NH_3	0,2 ppm HCl	0,2 ppm $C_4Cl_4F_6$
Irrevers. degradation rate @ 0.6 A/cm², µV/h	0	-208	+42	+20

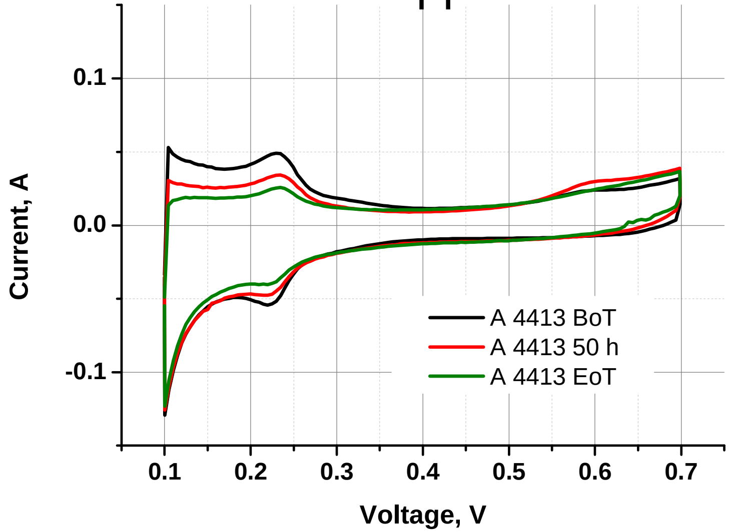
ANODE ACTIVE SURFACE EVOLUTION

Hydrogen

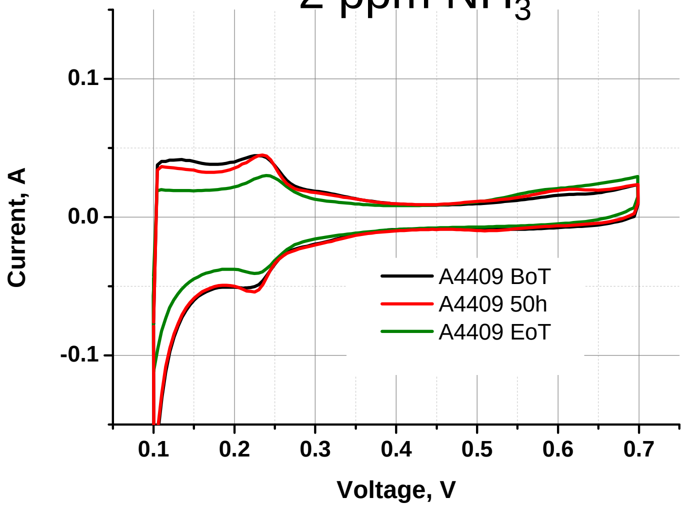
Pure H_2



0.2 ppm HCl



2 ppm NH_3



0.2 ppm $C_4Cl_4F_6$