FCH JU Projects Workshop

Degradation of PEM Fuel Cells
- experience exchange and discussions

Results from STAYERS project

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Content

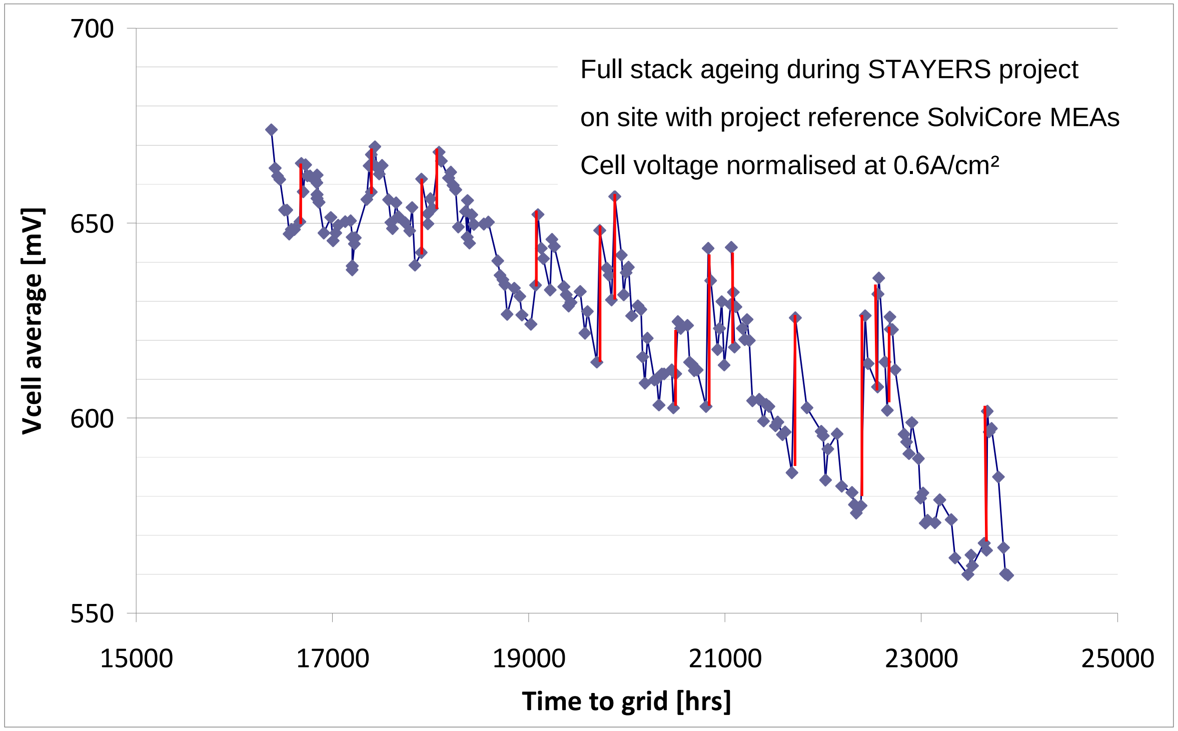
Components investigated in the presentation	Conditions applied
membrane	stationary @ 0.6A/cm² (SC) or 0.5A/cm² (Delfzijl)
MEA	humidification ca. 80% inlet
catalyst/electrode	Temperature 65°C

- **Comparison field test vs. lab test**
- **Understanding of the degradation patterns**
  - Reversible
  - Retrievable (also named as recoverable)
  - Irreversible
  - Possible causes of different degradation patterns?
- **Impurity tests**
  - Brief literature overview on NO_2 or SO_2 poisoning
  - Cathode: NO_2, SO_2
  - Anode: CO
- **Conclusion**

Comparison field test vs. lab test

Ageing in field test

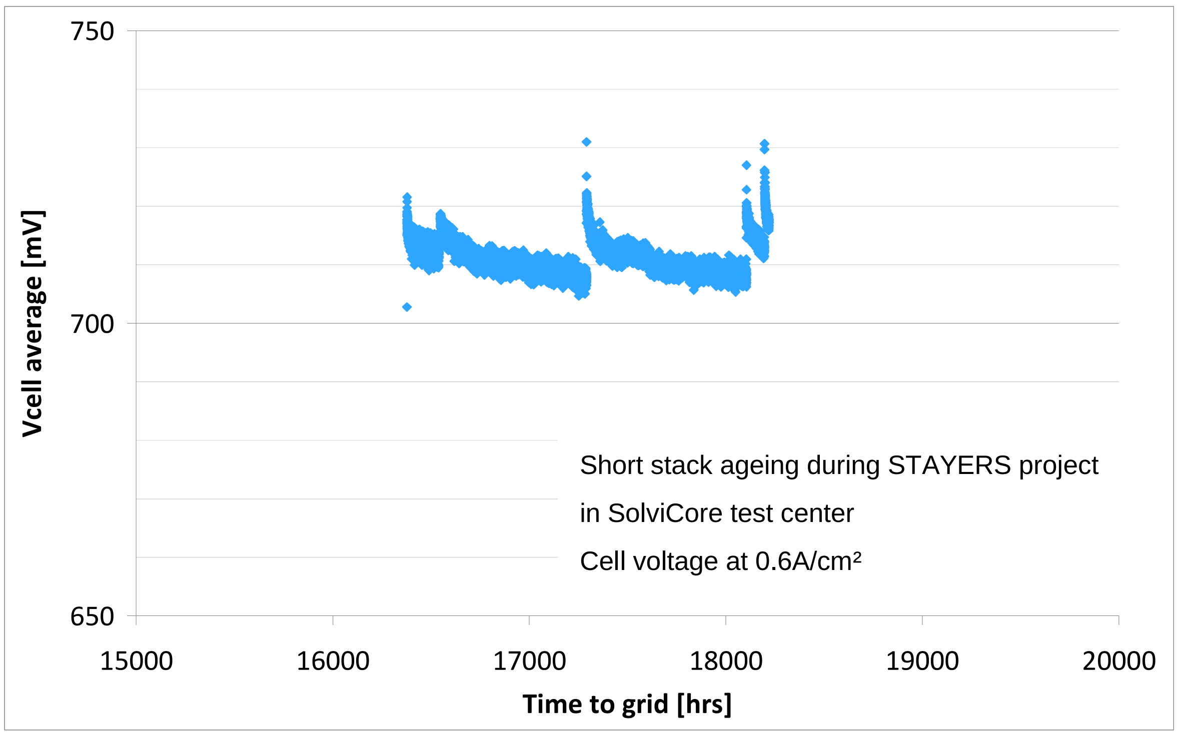
- **Stacks in field (i.e. Delfzijl PPP) can show**
  - High degradation rates
  - Saw-tooth effects after shut-down and restart



- **Similar behaviour can be observed in some customers test centers**

Ageing in lab test

- **In SolviCore test center, with same MEAs**
  - Degradation observed are lower,
  - Saw-tooth effect can be observed, too

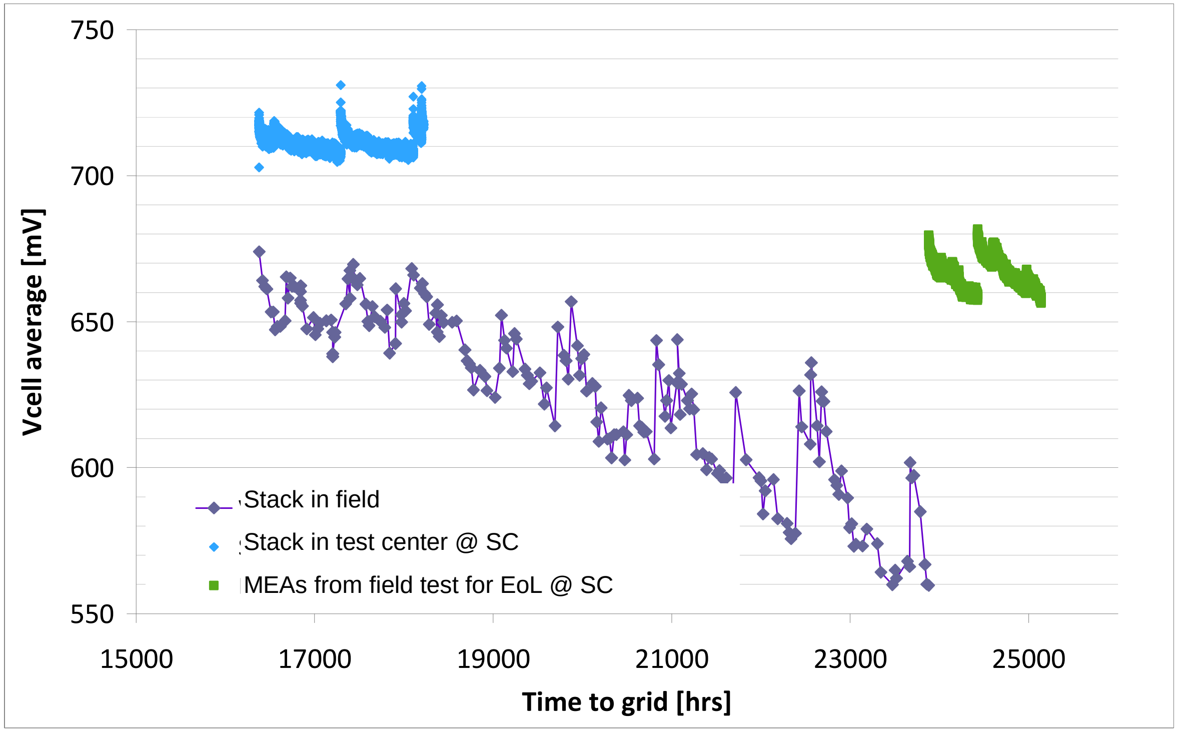


Comparison ageing in lab vs. field test

STAYERS

SolviCore Fuel Cell Technologies

- **Significantly different behaviours observed:**



- **After stack disassembly the MEAs have been re-assembled in small stack at SolviCore for EoL evaluation**
  - Stronger decay (saw tooth - reversible) after ageing
  - Higher performance than in field

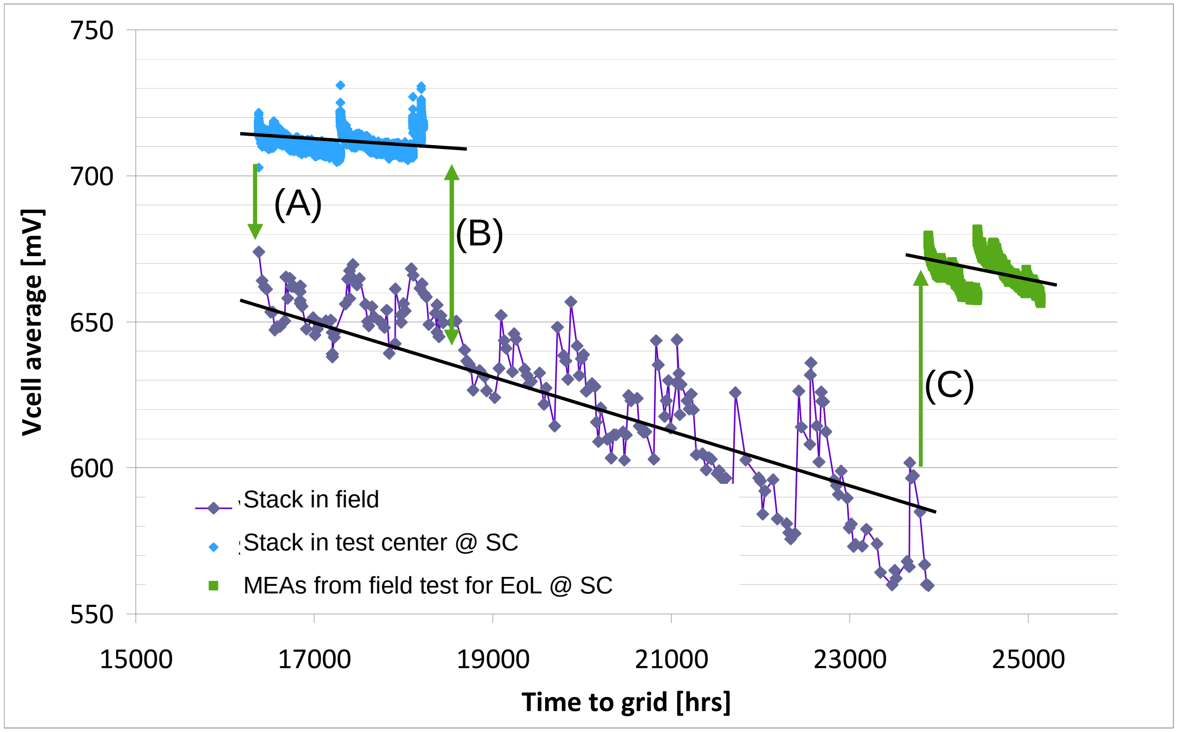
Comparison ageing in lab vs. field test

How to explain these findings?

(A) Performance gap at BoL

(B) Differences in degradation trends

(C) EoL performance gain in Lab



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Degradation patterns

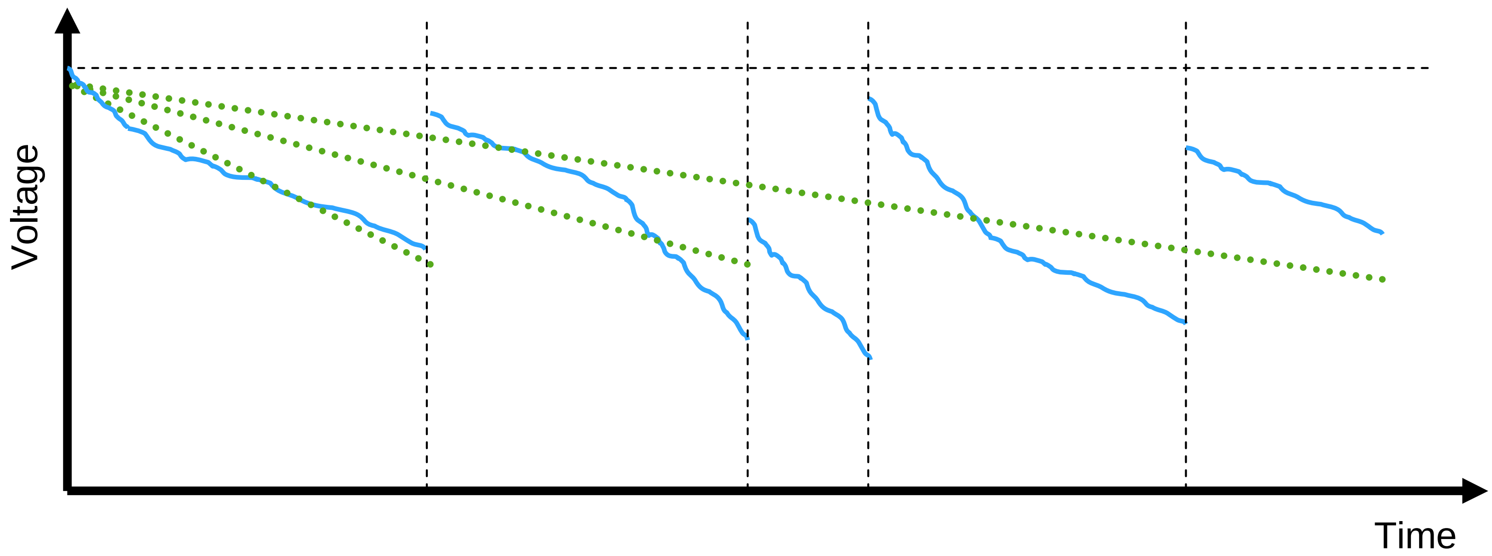
Degradation patterns analysis

- **Definitions**
  - Irreversible degradation: performance loss that will not be recovered (e.g. catalyst activity loss)
  - Reversible degradation: performance loss that will be simply recovered with simple stop and re-start (e.g. channel flooding)
  - Retrievable degradation: performance loss which can be recovered applying a specific protocol (e.g. impurities)

- **How to estimate degradation and lifetime – Suggestions:**
  - Case 1 - Trend line
  - Case 2 - Cell potential difference from BoL to EoT
  - Case 3 - Distinguish between reversible, retrievable and irreversible decays
  - Case 4 - Irreversible decays

Degradation patterns analysis

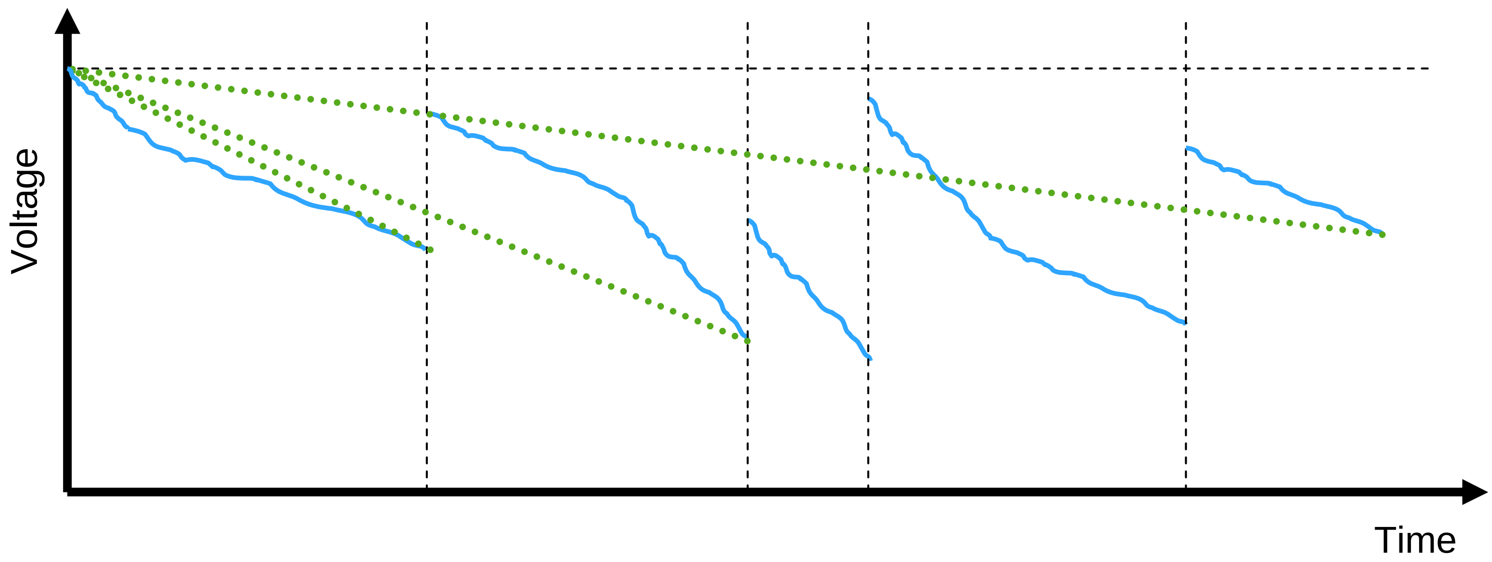
Case 1 - Trend line



Good mean value between reversible and irreversible

Degradation patterns analysis

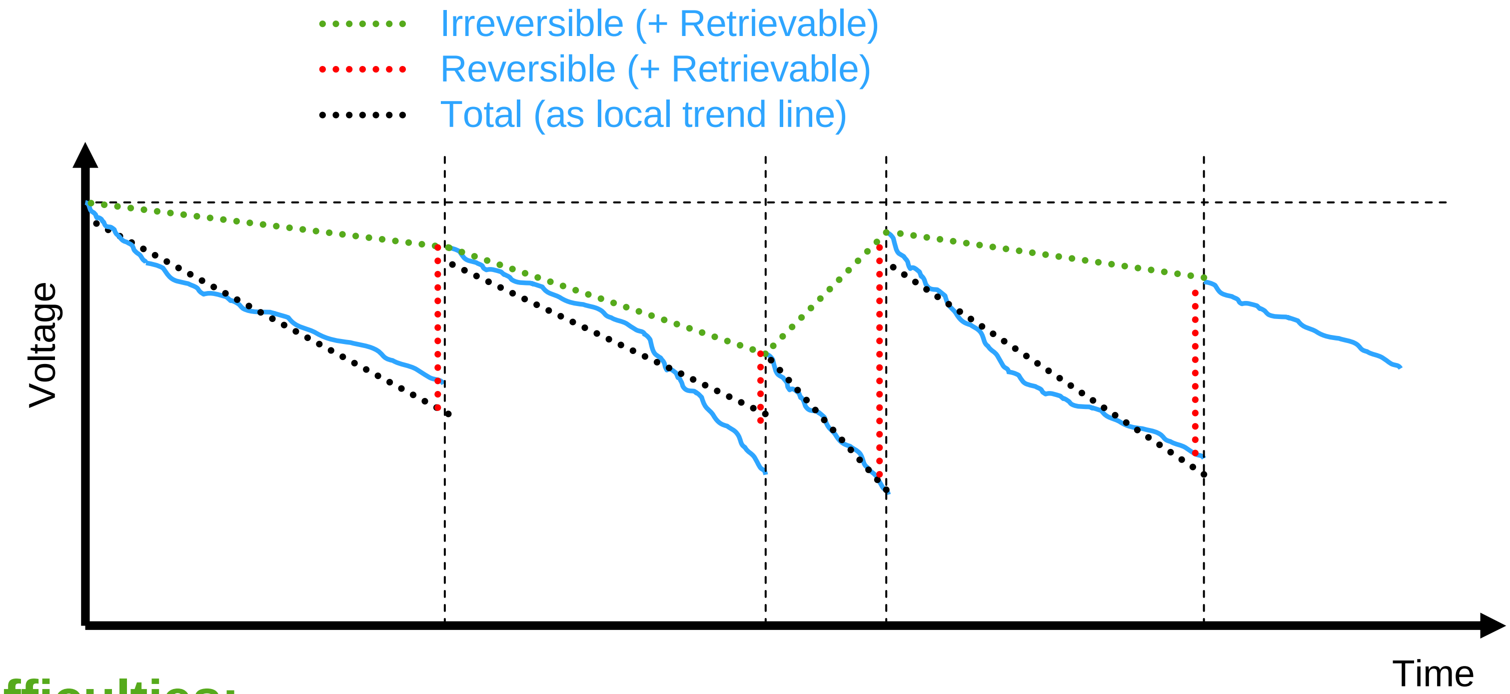
- **Case 2 - Cell potential difference from BoL to EoT**



- **Strongly influenced by the last hours of test**

Degradation patterns analysis

Case 3 - Distinguish between reversible, retrievable and irreversible decays

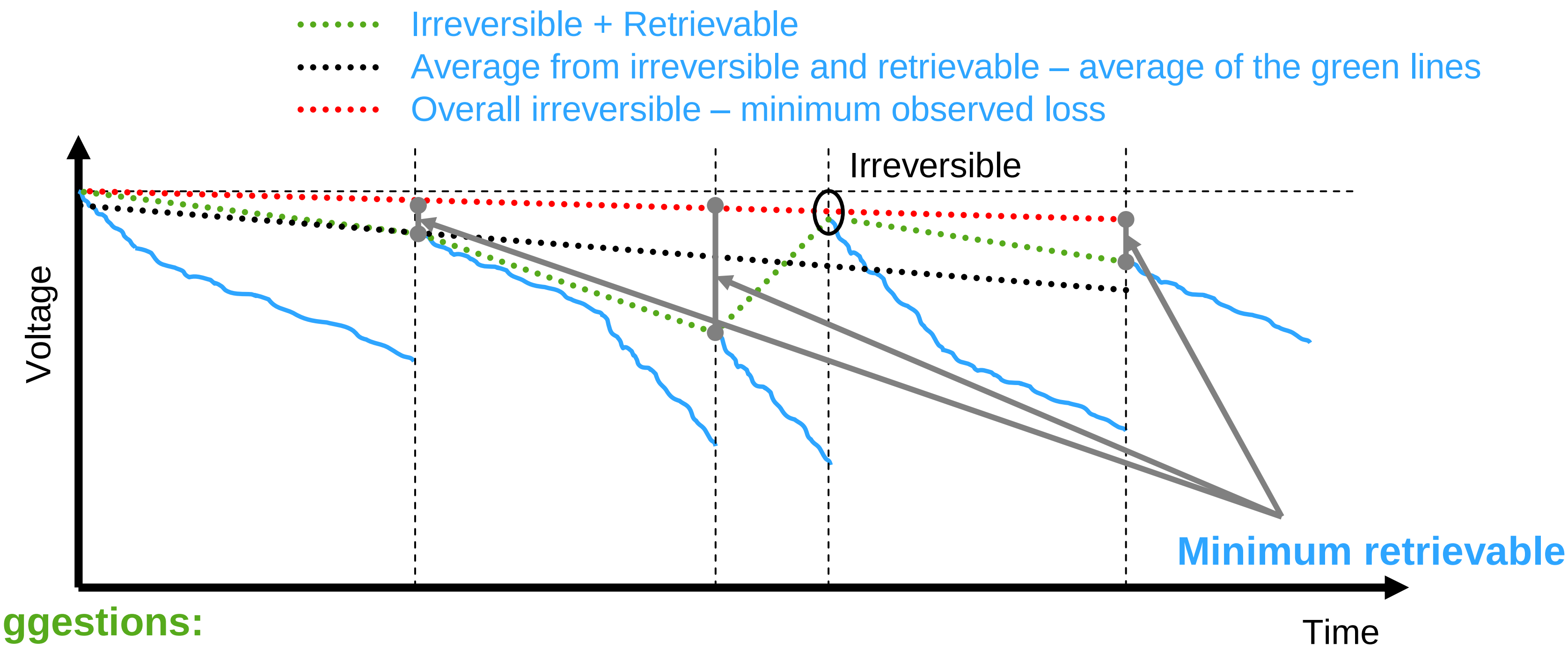


Difficulties:

- Will depend on several parameters like:
  - Shut-down protocol (controlled or uncontrolled)
  - Gas quality
  - Off-time (SO_2 and similar effects – see following slides)

Degradation patterns analysis

Case 4 – irreversible and retrievable decay as trend line



Suggestions:

- Use irreversible degradation (e.g. for purpose of lifetime prediction)
  - As the minimum delta (red curve)
  - But still depending on environment
- Use reversible and retrievable
  - as additional input to steer development
  - Not a predictive tool!

Possible causes of degradation?

- **For irreversible degradation**
  - MEA composition
    - Internal poisoning,
    - Change in key physico-chemical properties, etc.
  - Stack environment
    - Stack regulation
      - temperature,
      - fuel starvation,
      - load cycling, etc.
    - Irreversible poisoning (H_2S, cations)

- **For reversible degradation**
  - MEA composition (poisoning)
  - Stack environment
    - Anode and cathode gas quality
    - Stack regulation
      - Flooding, etc.

- **For retrievable (recoverable) degradation**
  - Stack control
    - Shut-down procedures

Impurity tests

Impurities: General

X.Cheng et al. / *Journal of Power Sources 165 (2007) 739-756*

Table 1
Major contaminants identified in the operation of PEM fuel cells

Impurity source	Typical contaminant
Air	N_2, NO_x (NO, NO_2), SO_x (SO_2, SO_3) NH_3, O_3
Reformate hydrogen	CO, CO_2, H_2S, NH_3, CH_4
Bipolar metal plates (end plates)	Fe^{3+}, Ni^{2+}, Cu^{2+}, Cr^{3+}
Membranes (Nafion®)	Na^{+}, Ca^{2+}
Sealing gasket	Si
Coolants, DI water	Si, Al, S, K, Fe, Cu, Cl, V, Cr
Battlefield pollutants	SO_2, NO_2, CO, propane, benzene
Compressors	Oils

NO_2 poisoning in literature

R.Mohtadi et al. / *Journal of Power Sources (2004)*

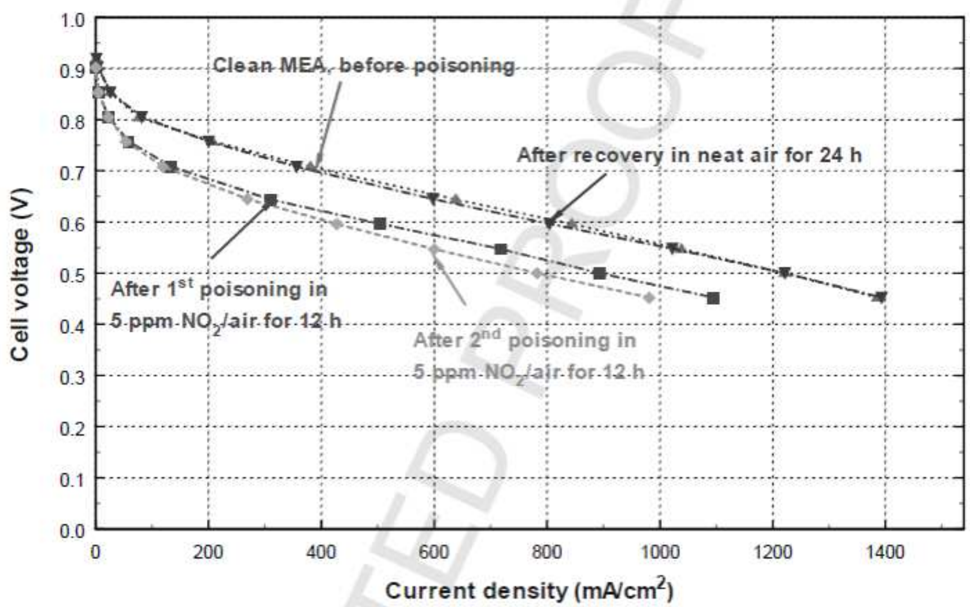


Fig. 4. Polarization for steady state performance showing the effects of 5 ppm NO_2/air.

Decay is reversible going back to neat air.

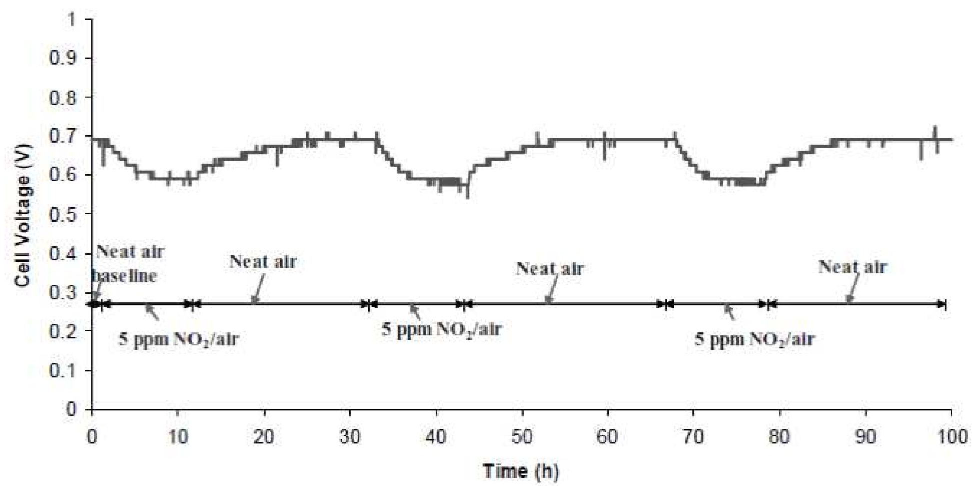


Fig. 16. Initial durability tests in 5 ppm NO_2/air.

NO_2 poisoning in literature

R.Mohtadi et al. / *Journal of Power Sources (2004)*

- **CV does not show any oxidation peak. It is supposed that NO2 poisons the ionomer after ammonia formation:**

$$NO_2(g) + 8H^+ + 7e^- \rightarrow NH_4^+ + 2H_2O, \quad E^o = +0.897$$

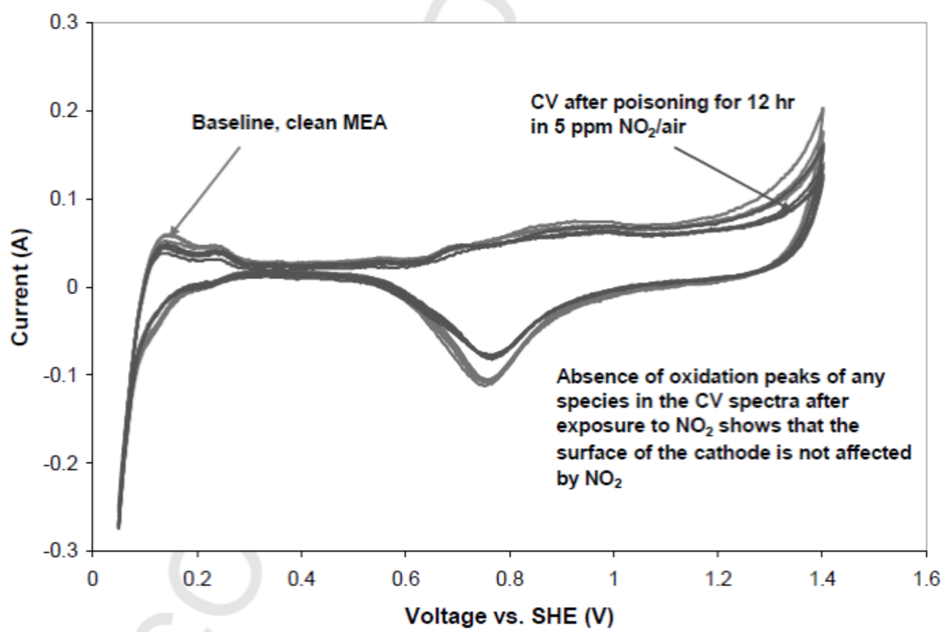


Fig. 6. Cyclic voltammetry spectra obtained after cathode exposure to 5 ppm NO_2/air.

SO_2 poisoning in literature

DOE Hydrogen Program FY 2005 Progress Report

VII.I.4 Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

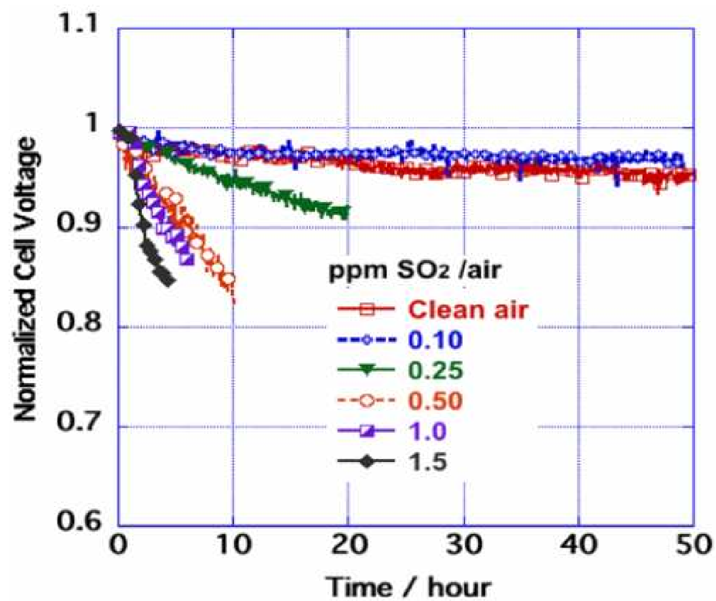


Figure 1. Effect of SO_2 Concentration on Cathode Performance at 80 °C (A total of 0.010 mmol of SO_2 was injected at the cathode at each concentration. Cell size: 50 cm^2; anode and cathode loadings (mg Pt/cm^2): 0.21 and 0.22 respectively. Cell run at 0.6 A/cm^2 constant current.)

- **SO_2 has a much stronger influence on performance than NO_2**

SO_2 poisoning in literature

DOE Hydrogen Program FY 2005 Progress Report

VII.I.4 Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

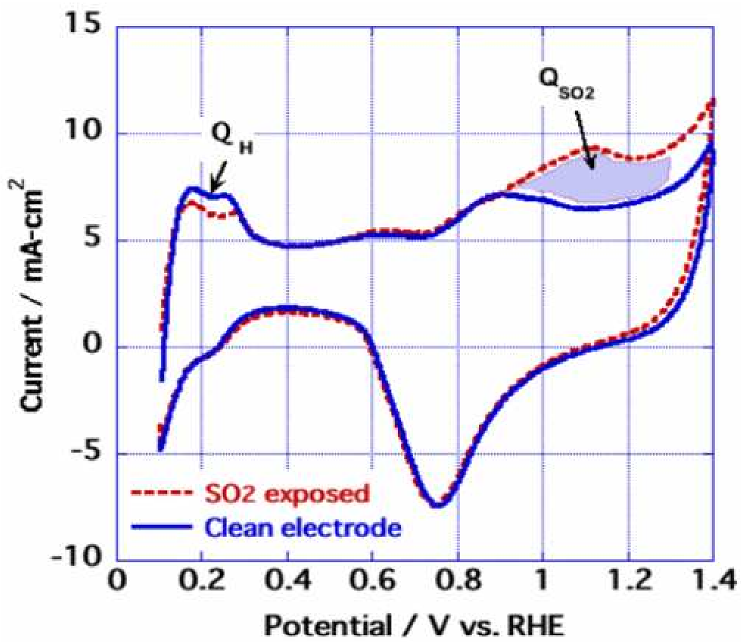


Figure 2. CVs of a Cathode Electrode Exposed to 1.5 ppm SO_2 for 4.3 hr at 80 °C (The CV of the clean electrode is also shown for comparison. Cell size: 50 cm^2; anode and cathode loadings (mg Pt/cm^2): 0.21 and 0.22 respectively. Scan rate: 50 mV/s.)

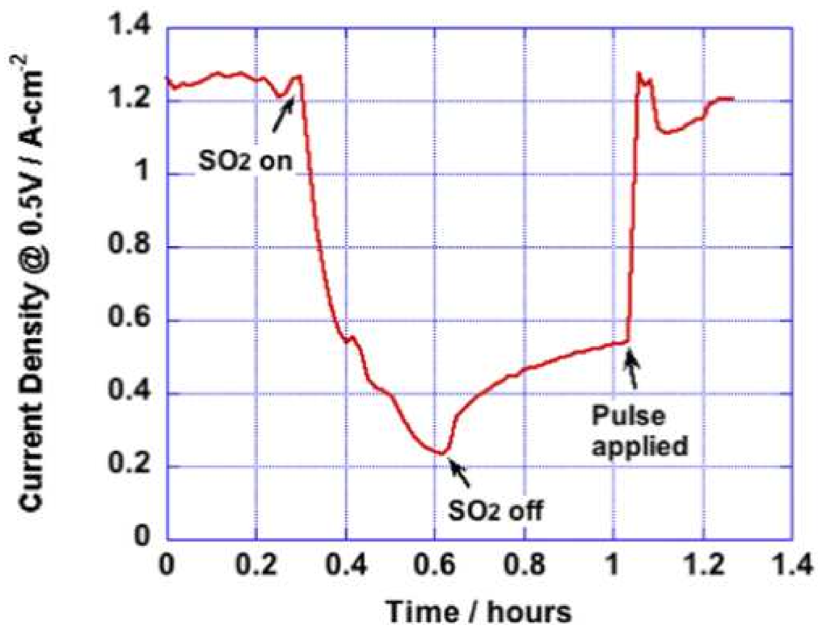
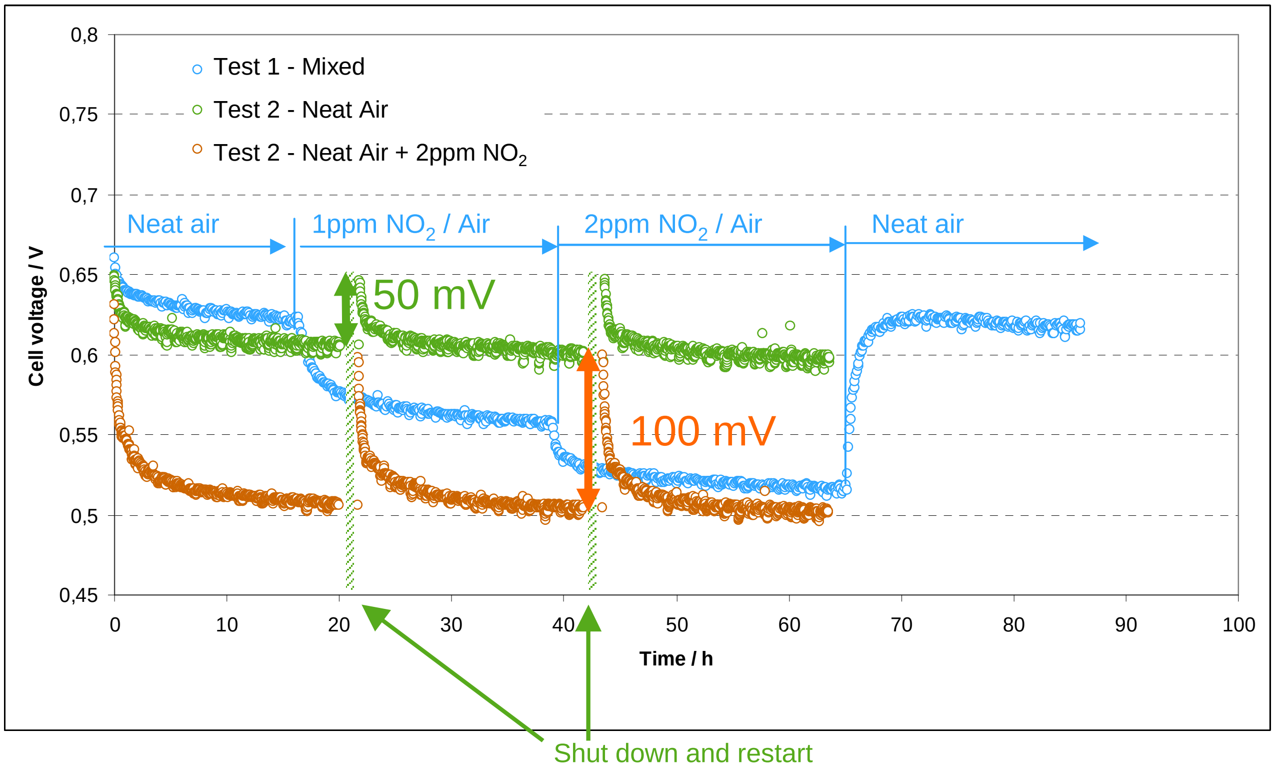


Figure 5. Cleaning a Cathode Poisoned with 10 ppm SO_2 at 80 °C (A 1.4 volt pulse was applied with an external power supply for 5 seconds. Anode and cathode loadings in mg Pt/cm^2: 0.18 and 0.22 respectively. Cell size: 5 cm^2.)

- **A cleaning effect of the cathode electrode can be obtained applying a voltage of 1.4 V**

NO_2 poisoning test at SolviCore

- **Comparison of neat Air vs. NO_2/Air on project reference SolviCore MEA (not impurity tolerant)**



- **The loss is fully reversible switching back to neat air**
- **Even with neat air, different NO_2 concentration could explain initial performance differences**

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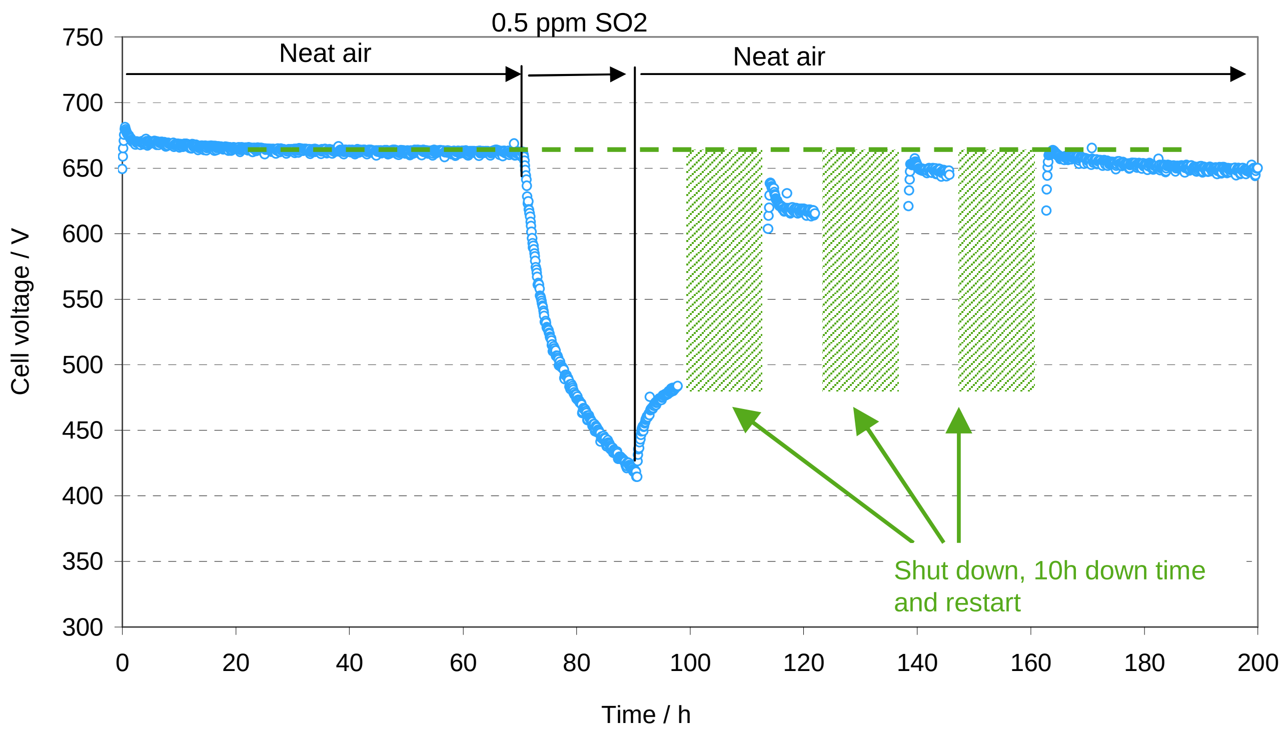
SO_2 poisoning test at SolviCore

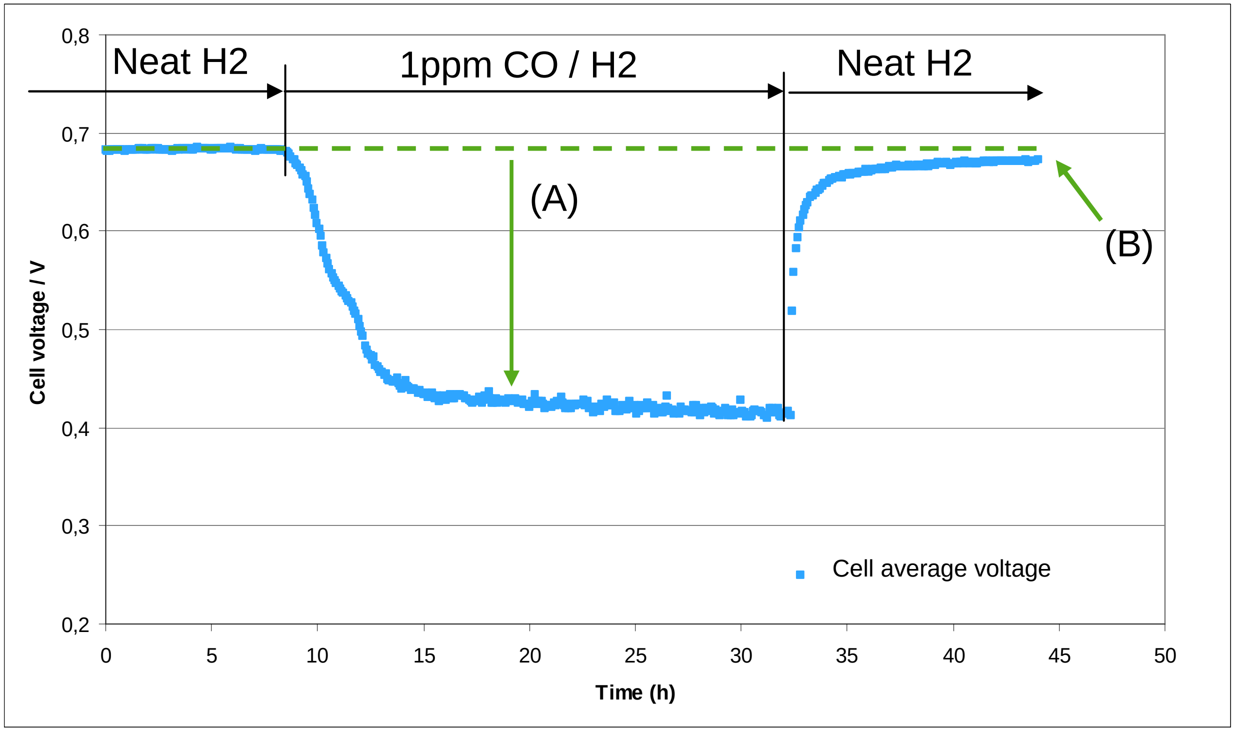
- **Comparison of Neat Air vs. SO_2/Air on project reference SolviCore MEA (not impurity tolerant)**



- **The loss can be recovered with dedicated shut-down / down time procedures**

CO poisoning test at SolviCore

Effect of 1ppm CO on project reference SC Anode (not impurity tolerant)



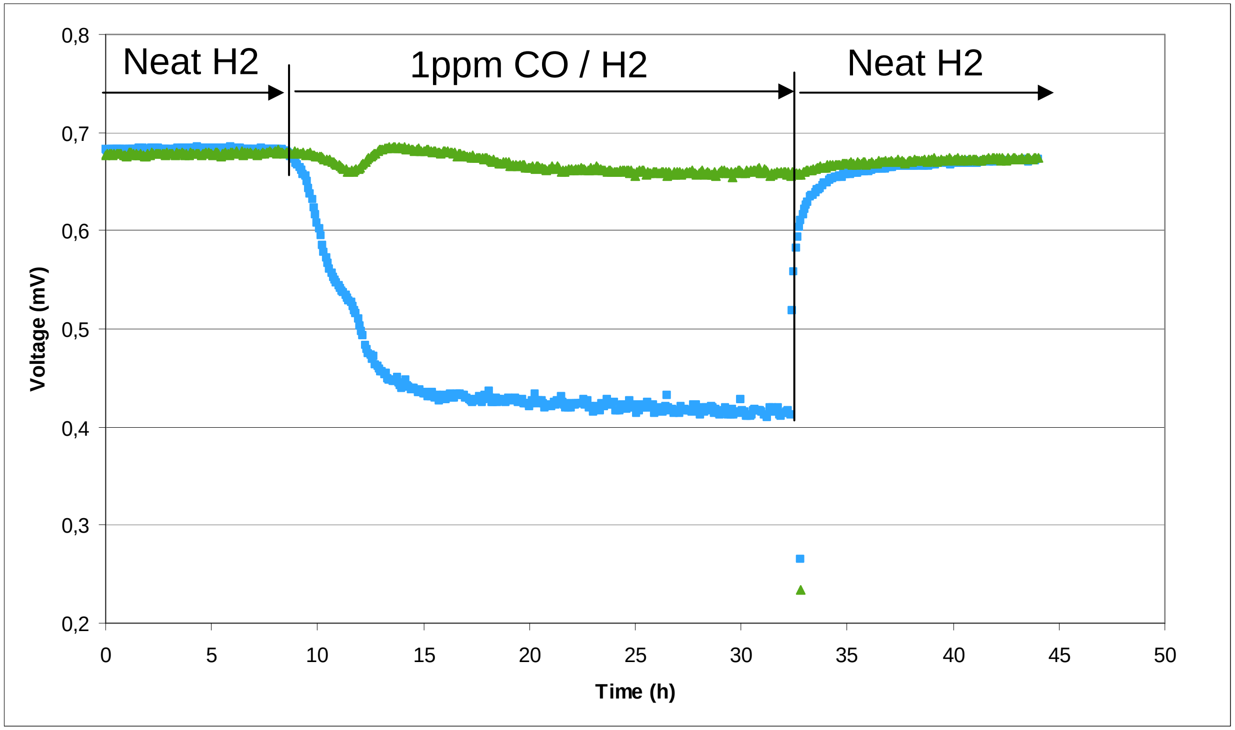
- **Reversible loss of ca. 250mV**
- **Irreversible loss of ca. 10mV**

Conclusion

Conclusion

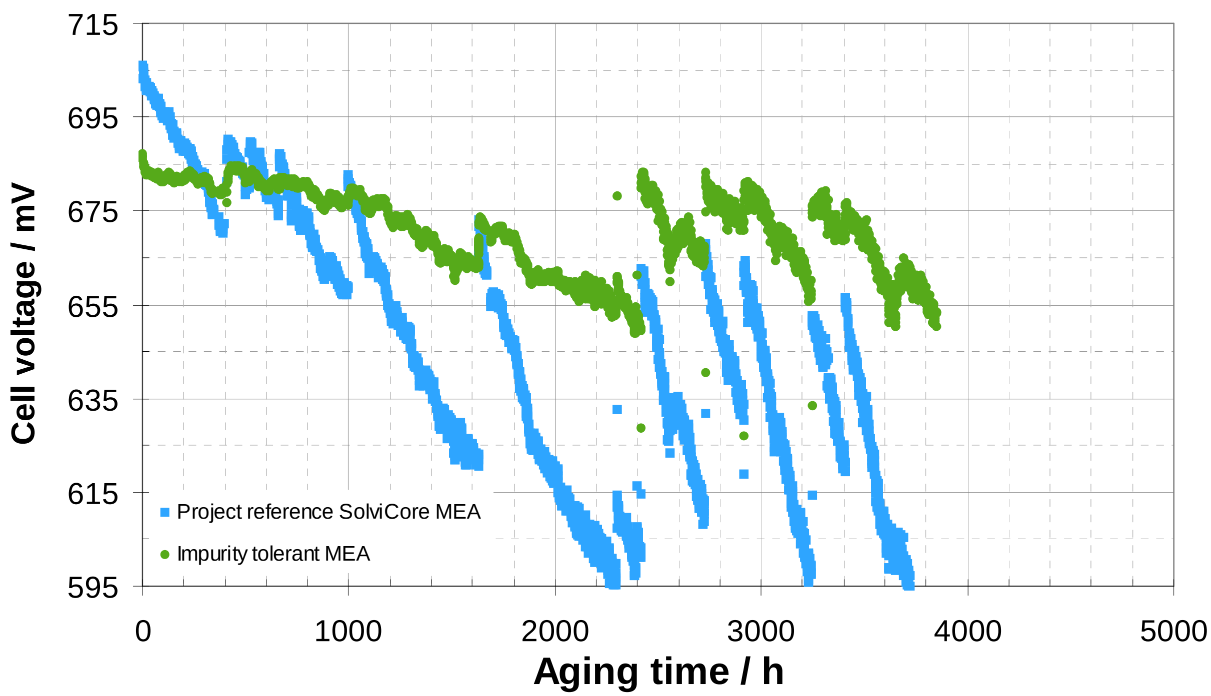
- **Degradation has to be addressed on system side as well as on MEA side**
- **On MEA side:**
  - Solutions possible
    - Catalyst type
    - Catalyst layer properties and composition
  - Focus: keep cost compatible with market request
- **On System side:**
  - Better filtering capacity
  - Better recovery protocols after “pollution peaks”
  - Optimise system conditions to reduce reversible and irreversible degradations

Example of SolviCore CO-tolerant anode (for 1ppm)



Conclusion

Improvement in lifetime using impurity tolerant MEA



Lifetime prediction based on irreversible degradation:

- Project reference SolviCore MEA: 6.500h before Nedstack EoL criteria
- Impurity tolerant MEA: 31.000h before Nedstack EoL criteria

Conclusion

Main degradation mechanisms (irreversible/reversible)		Further details
Contamination (A/C)	**2**	A: CO, C: SOx, NOx --> any coumpounds not identified yet will be impacted by ECSA losses
ECSA loss (A/C)	1	particle growth/Pt dissolution or carbon corrosion?
increase electronic resistance (A/C)	3	electronic vs. proton resistance
membrane - increase of proton resistance	4	
membrane - increase in H2 X-over	6	
flooding / loss of hydrophobicity (A/C)	5	Guess: Method missing

Acknowledgements

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Thank you for your attention

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