Mitigation of PEMFC Degradation upon Freeze-Thaw Cycling using a Methanol-Water Solution as Antifreeze

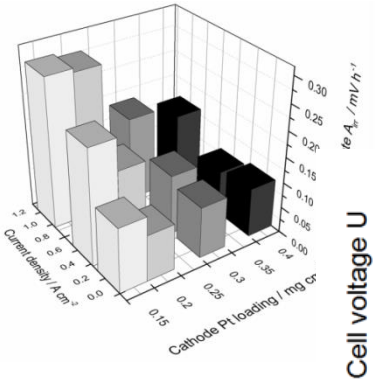
Florian Knorr, Daniel Garcia Sanchez, Johannes Schirmer, Pawel Gazdzicki, K. A. Friedrich

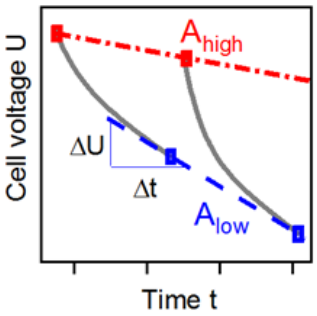
German Aerospace Center (DLR), Institute of Engineering Thermodynamics,
70569 Stuttgart, Germany

Contents

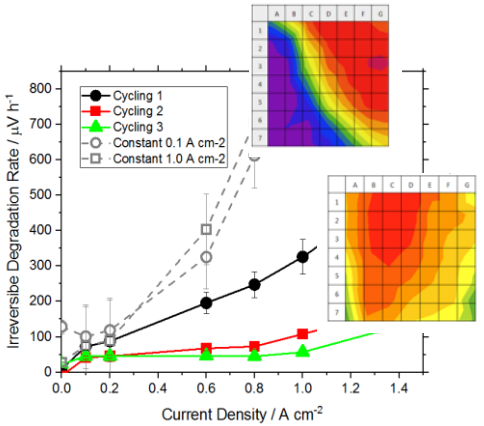
- Introduction
- F/T cycling
- Start-up procedures involving antifreeze
- Conclusions

Durability and Performance of PEMFC





- Durability and performance versus Pt loading including PGM-free electrodes
- Impact of Pt-loading on reversible and irreversible degradation and recovery of reversible losses
- Linking performance losses with local operation conditions, SoH monitoring
- **Investigate impact of stressors on durability** and development of specific in-situ AST
  - **Impact of F/T cycling on durability**
  - **Start up at T < 0°C**
  - **Mitigation of degradation due to F/T cycling**



Freezing as stressor for PEMFC

Freezing water in the cell cause damage to the MEA components

⇒ *Required to mitigate freezing*

- Getting rid of water before bringing cell to T < 0°C
  (→ purging cell by dry gas)
- Mitigate freezing of water when starting at T < 0°C
  (→ active heating, apply low voltage)

Alternative: flood cell by alcohol-water solution to avoid freezing

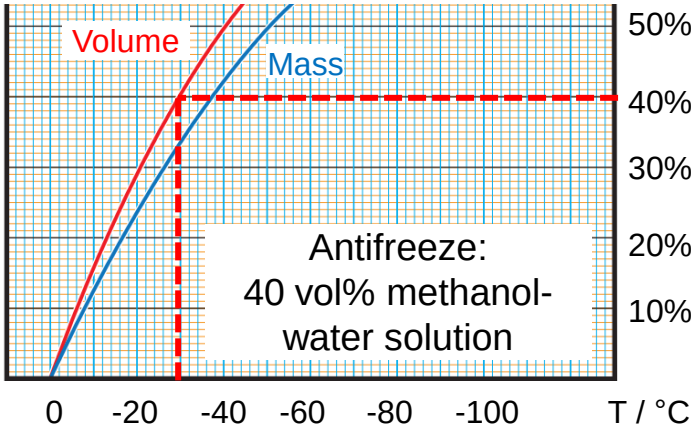
Journal of The Electrochemical Society, **151** (5) A661-A665 (2004)
0013-4651/2004/151(5)/A661/5/$7.00 © The Electrochemical Society, Inc.

Effects of Water Removal on the Performance Degradatio of PEMFCs Repetitively Brought to <0°C

EunAe Cho,[a] Jae-Joon Ko,[b,d] Heung Yong Ha,[a,*] Seong-Ahn Hong,[a] Kwan-Young Lee,[b] Tae-Won Lim,[c] and In-Hwan Oh[a,z]

[a]*Fuel Cell Research Center, Korea Institute of Science and Technology, Seongbuk-ku, Seoul 136-791, Korea*
[b]*Department of Chemical and Biological Engineering, Korea University, Seongbuk-ku, Seoul 136-701, Korea*
[c]*Hyundai Motor Company, Fuel Cell Vehicle Team, Namyang-myun, Whasung-gun, Kyunggi-do 445-850, Korea*

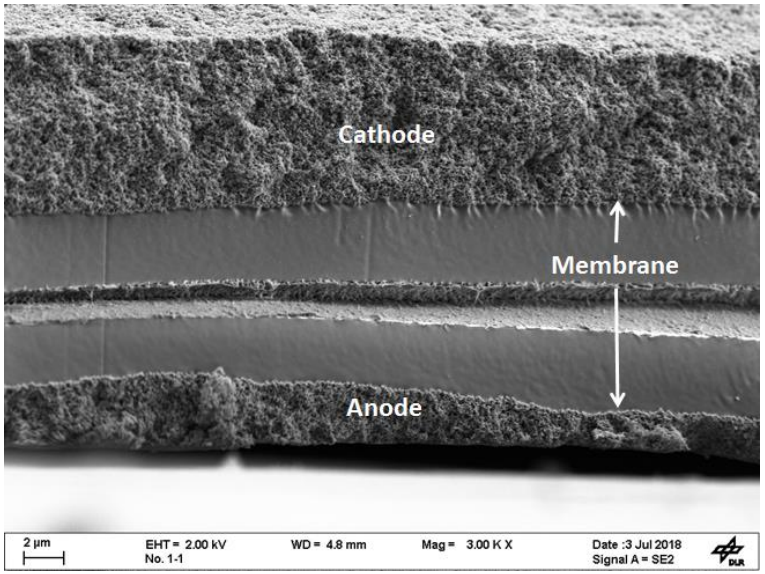
http://www.novosolution.ca/images/Freezing-Points-Methanol.pdf



Experimental setup

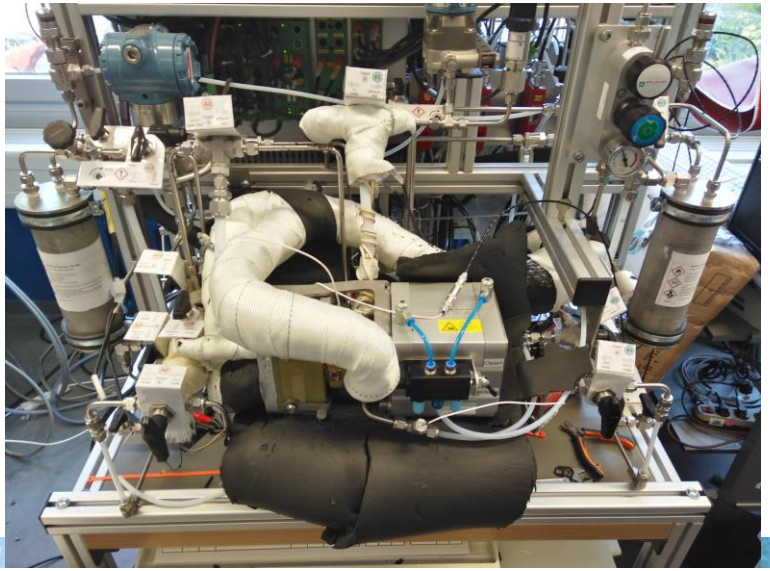
MEA

Parameter	Anode	Cathode
Active area	5 x 5 cm^2	
Catalyst	Pt/C or PtRu/C	Pt/C
Pt loading	0.1 mg cm^{-2}	0.25 mg cm^{-2}
Membrane	PFSA, 10 micron	



Test conditions

Parameter	Anode	Cathode
Cell temp. / °C	80	
Gases	H2	Air
RH	100%	100%
Stoich.	1.3	1.5
Pressure / bar_a	2.5	2.3



Test bench for F/T cycling with MeOH as antifreeze

F/T cycling and conditioning procedures

80°C — PEMFC operation

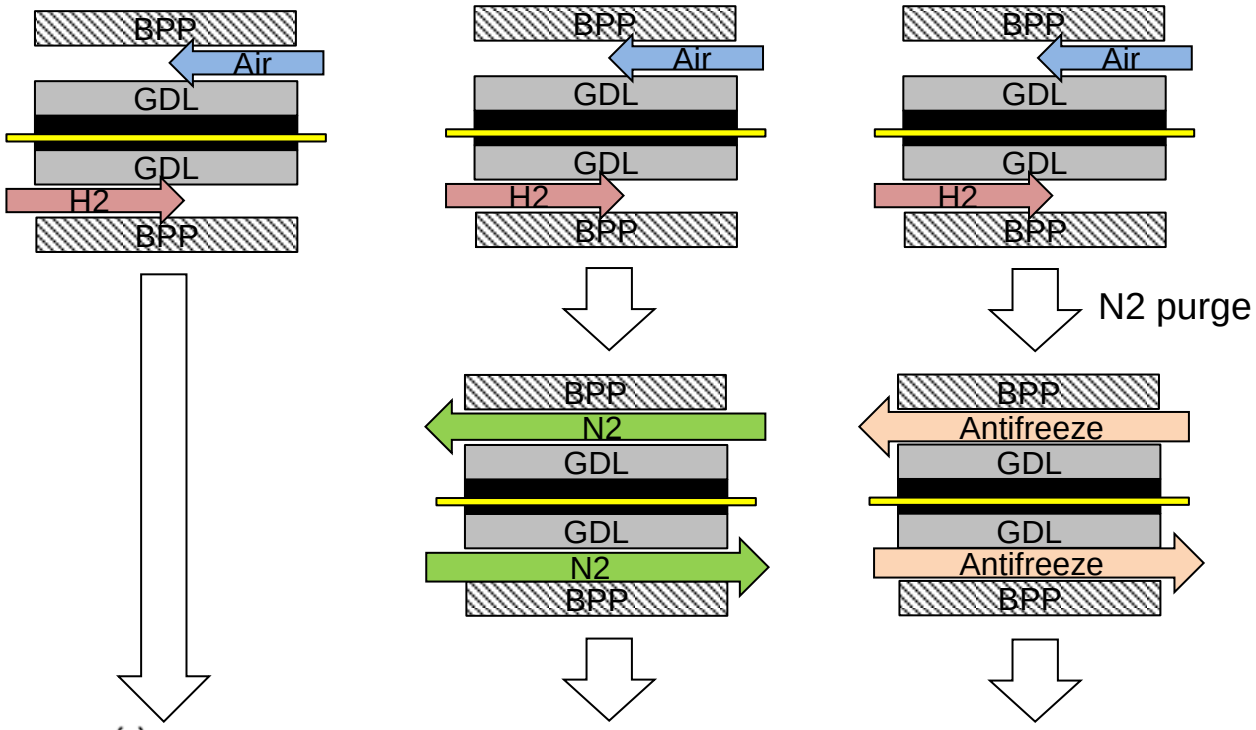
>0°C — Stop & conditioning

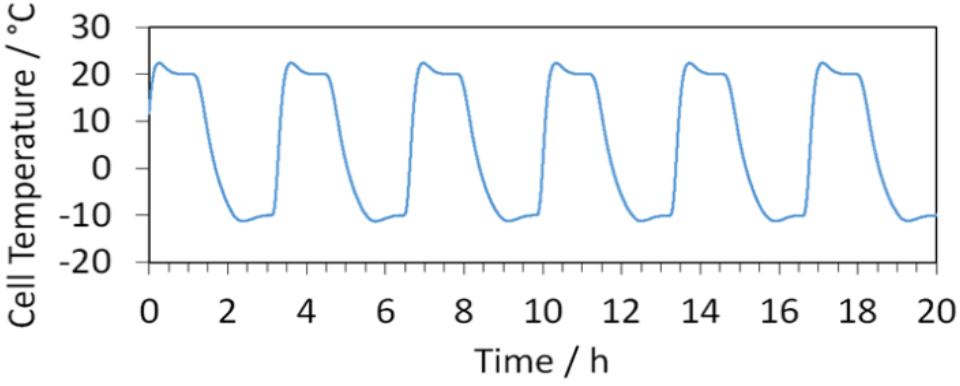
<0°C — F/T cycling

No conditioning

Purging with dry N_2

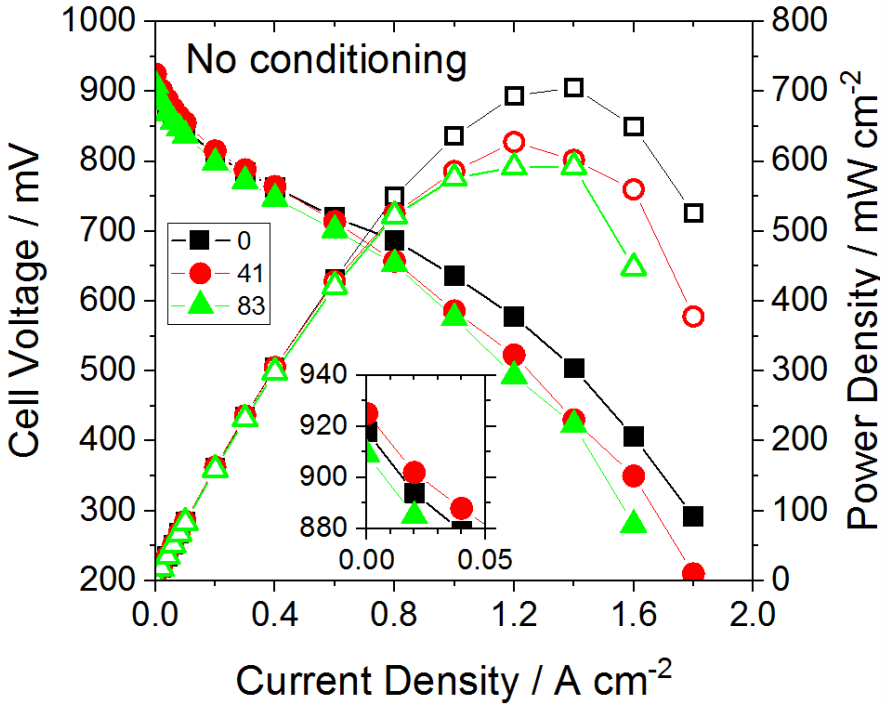
Antifreeze

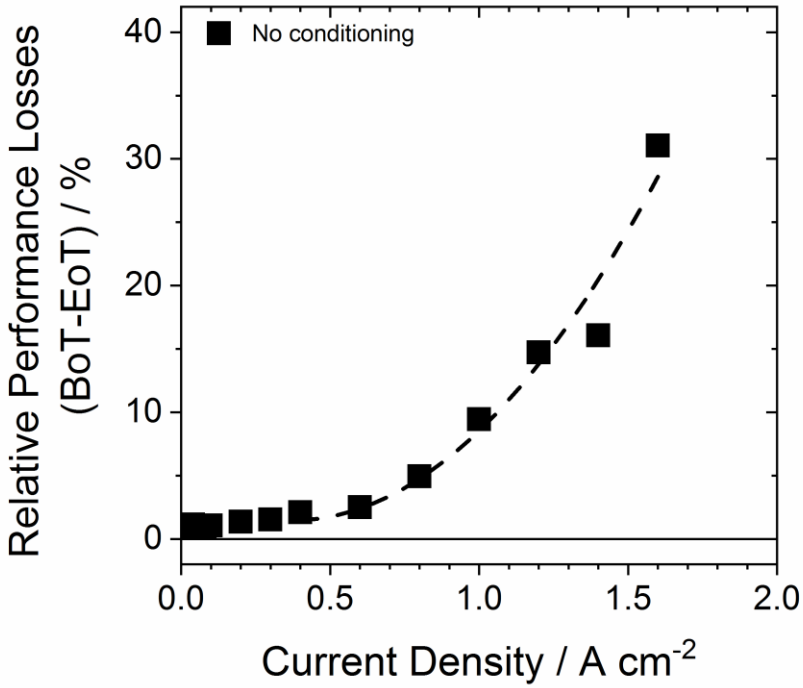




F/T cycling tests (I)

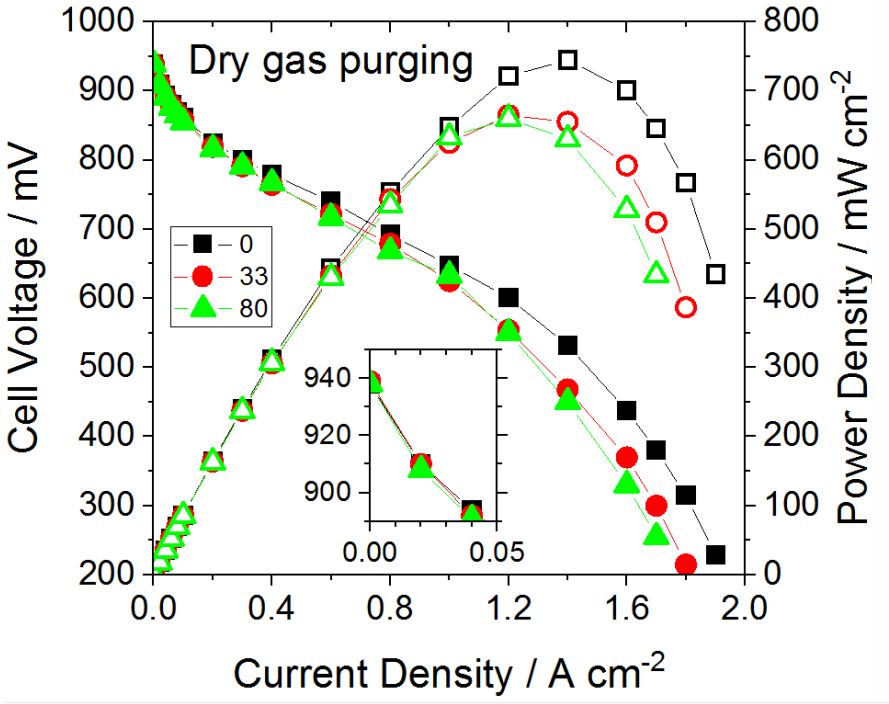
No conditioning

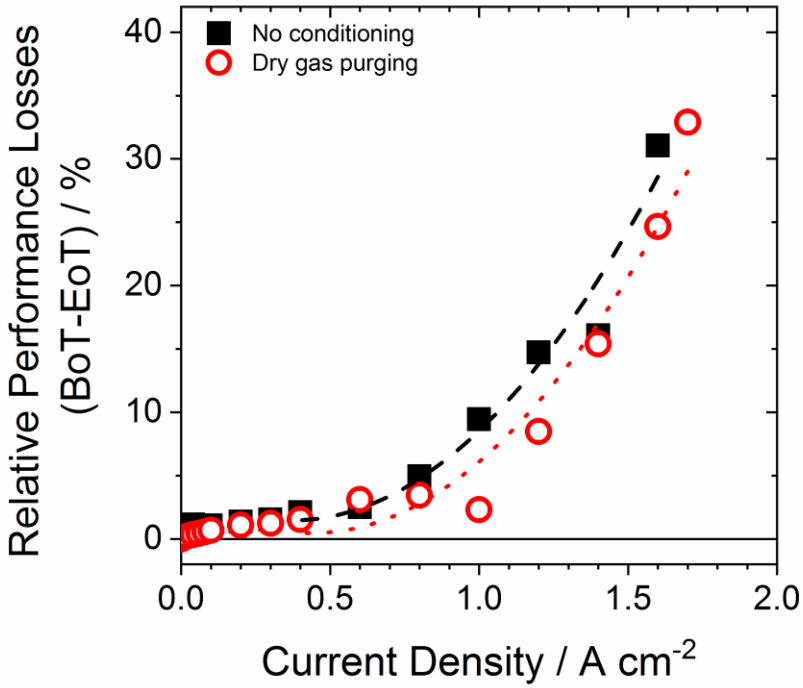




F/T cycling tests (II)

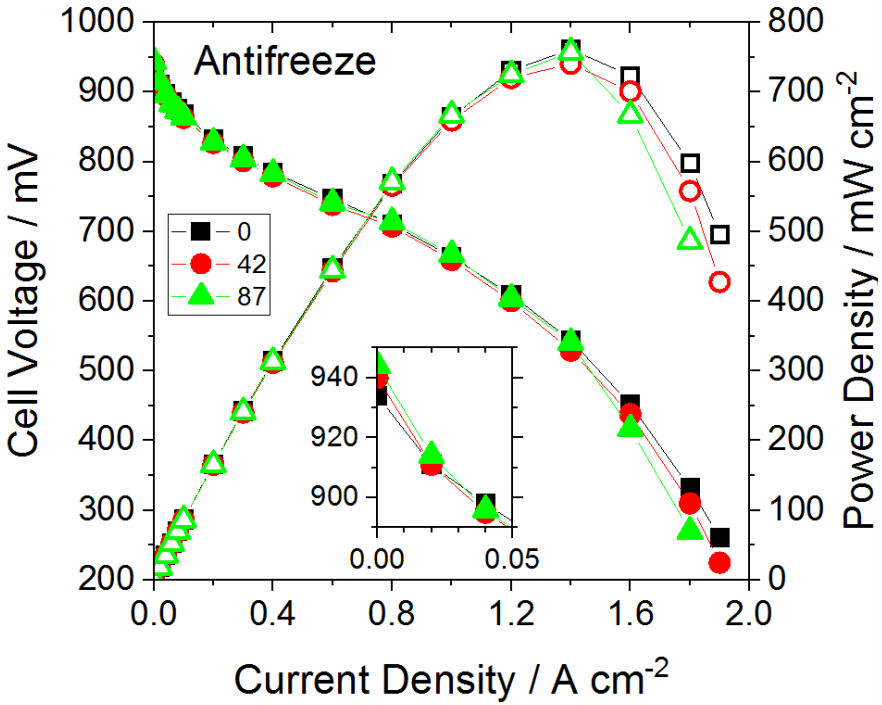
Dry gas purging

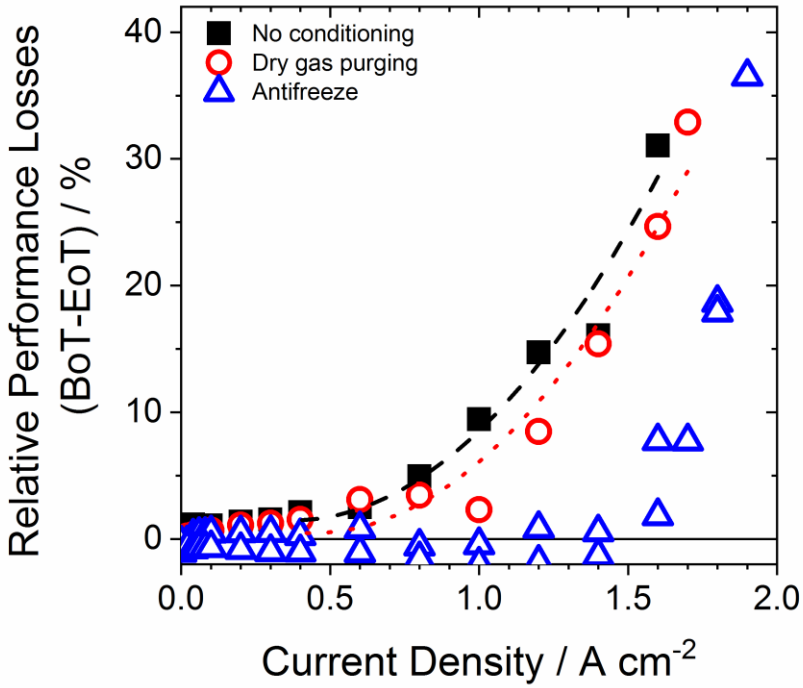




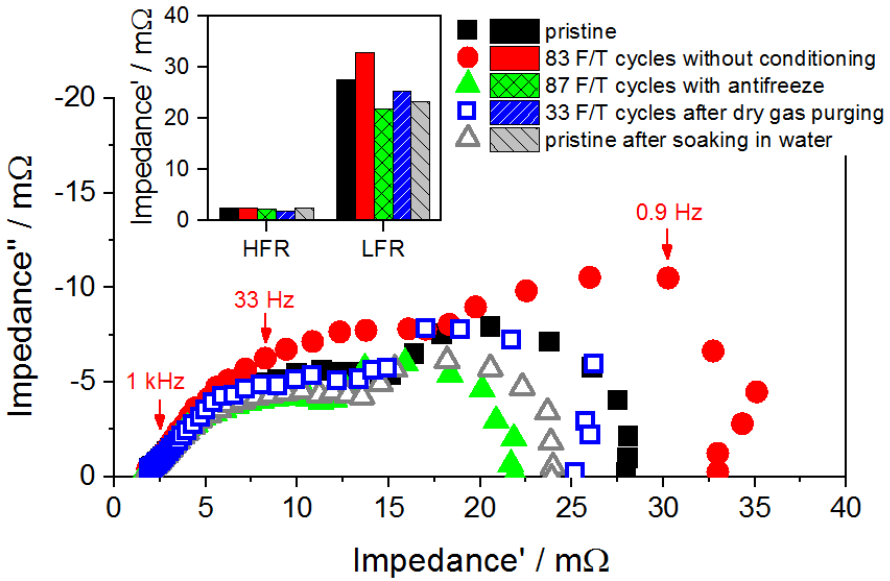
F/T cycling tests (III)

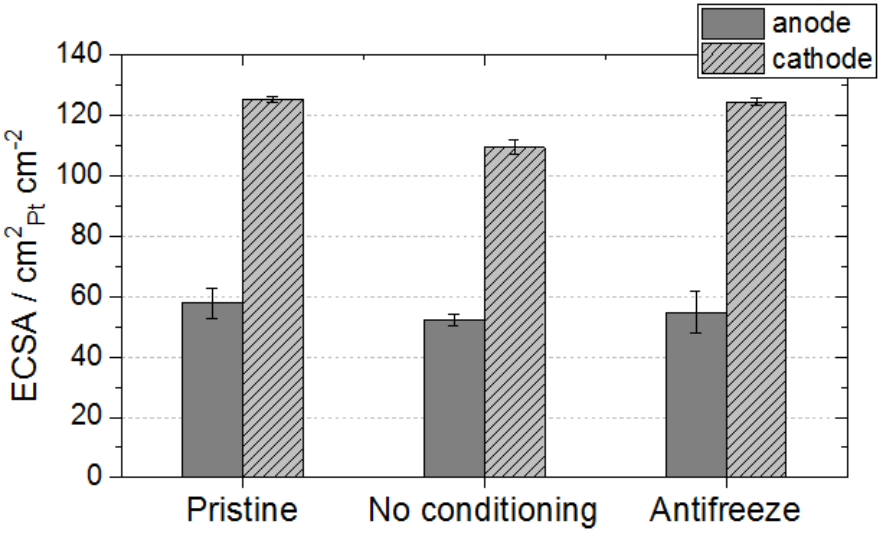
Antifreeze





Sample analysis

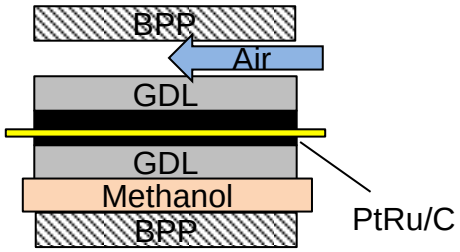




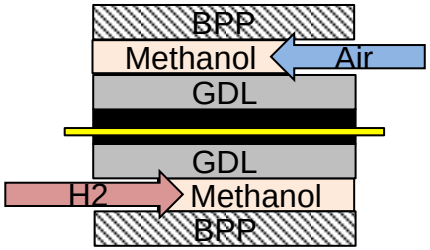
Start-up procedures involving antifreeze

T = -10°C

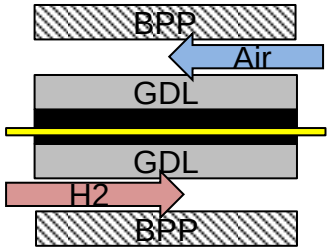
DMFC mode



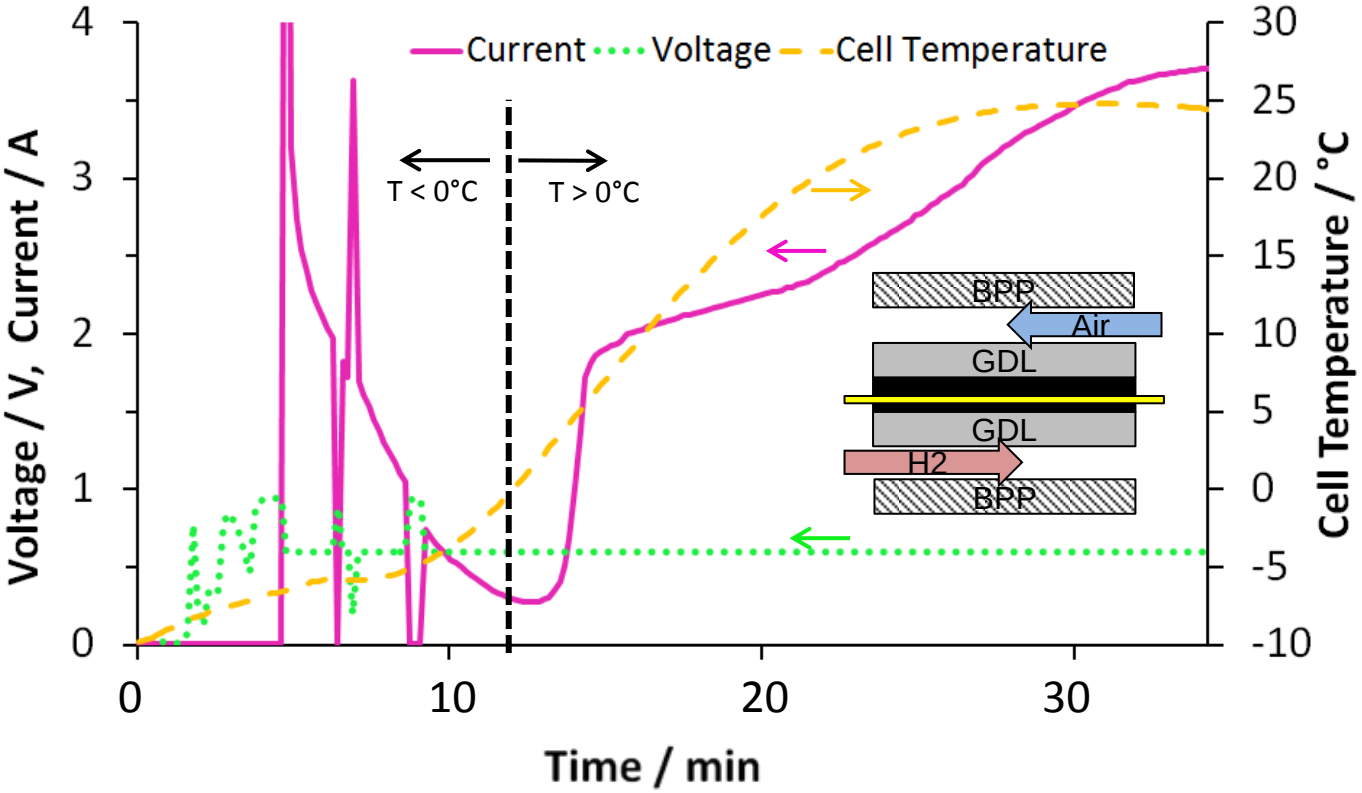
PEMFC mode with antifreeze



PEMFC mode without antifreeze

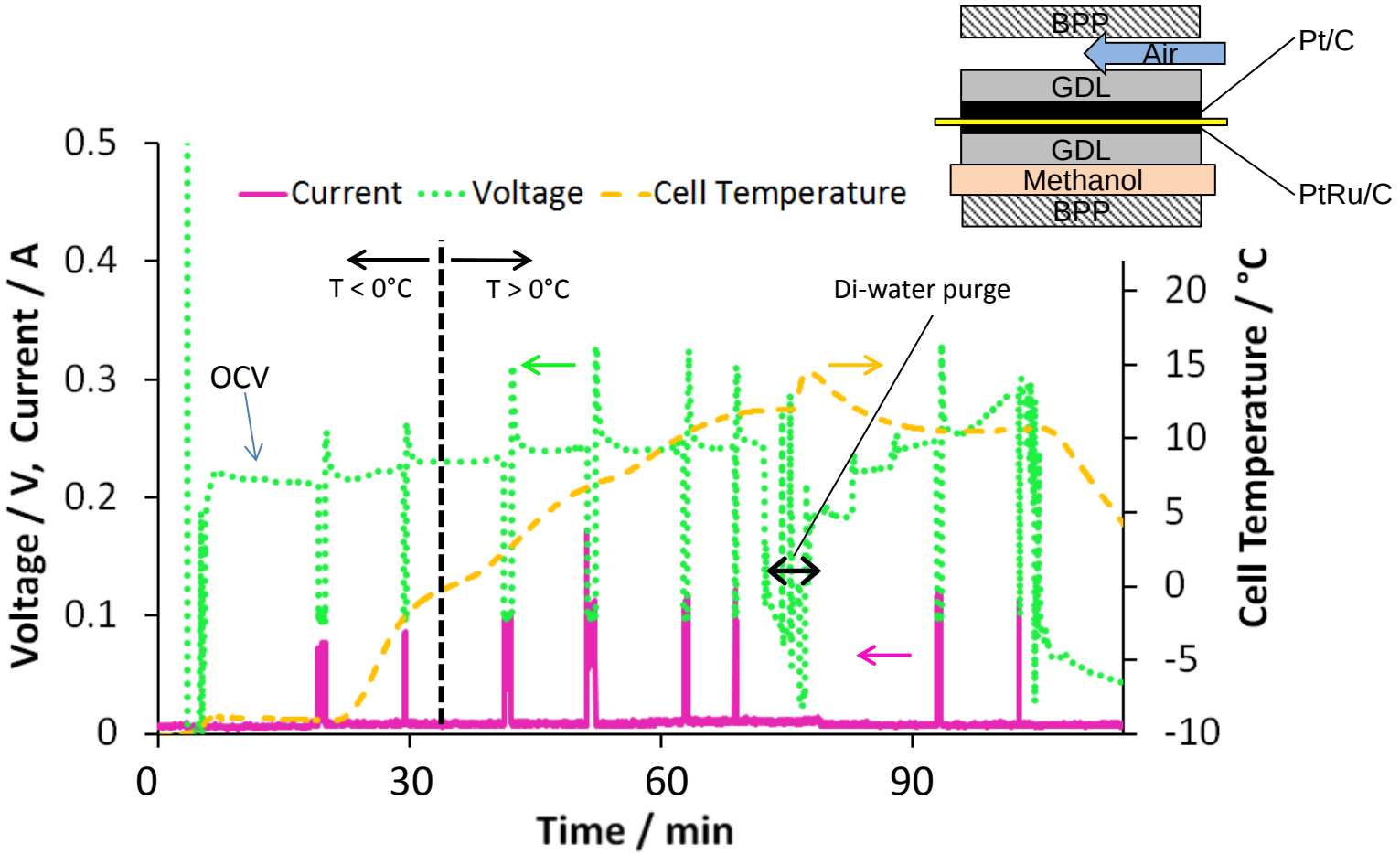


Start-up in PEMFC mode without antifreeze



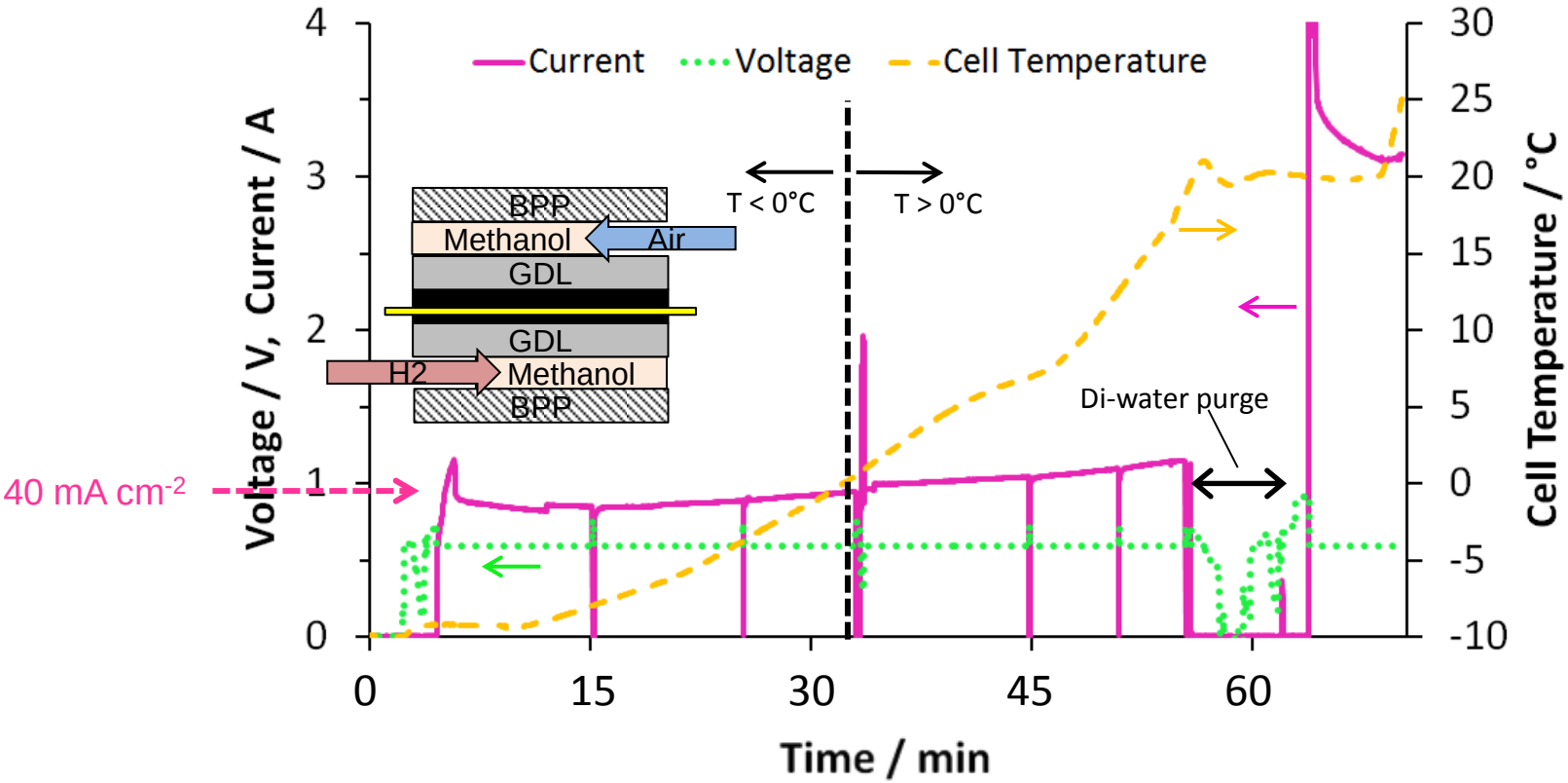
Rapid performance drop due to icing at T < 0°C

Start-up in DMFC mode



Problem: **low anodic PtRu loading** and a **thin membrane** of used MEA do not allow to handle poor methanol oxidation kinetics and mitigate methanol cross over, respectively.

Start-up in PEMFC mode with antifreeze



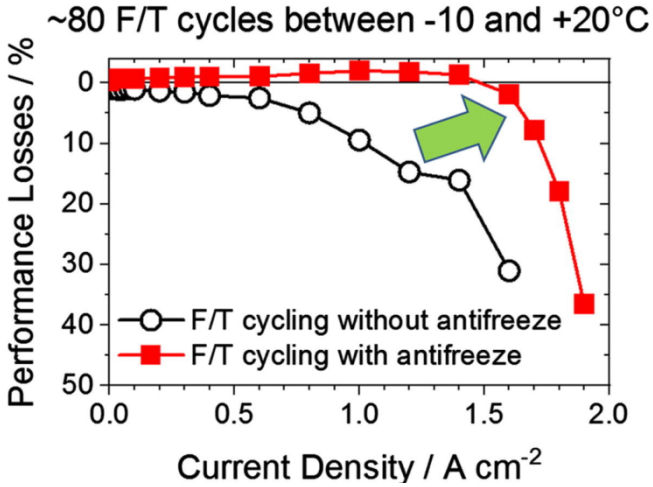
Successful cold start (< 30 s to 50% power) carried out in a stack by using a conventional start-up (drying with N2 before freezing) shows initial current of **80–120 mA cm^{-2}**

If successful cold start is possible using antifreeze, it is expected that residual methanol is removed due to evaporation at higher temperature and by drag with product water

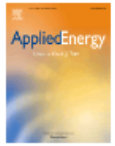
Conclusions

- Antifreeze strongly reduces performance degradation during F/T cycling: no degradation of peak performance
- Residual antifreeze allows continuous PEMFC operation at sub-zero temperatures
- Residual antifreeze reduces cell performance at T > 0°C

Antifreeze will be tested in PEMFC stack as next step within INN-Balance Project



ELSEVIER
Applied Energy
Volume 238, 15 March 2019, Pages 1-10



Methanol as antifreeze agent for cold start of automotive polymer electrolyte membrane fuel cells

Florian Knorr [a], Daniel Garcia Sanchez [a], Johannes Schirmer [a], Pawel Gazdzicki [a] ✉, K.A. Friedrich [a, b]

Show more

https://doi.org/10.1016/j.apenergy.2019.01.036

Thank you for your attention

Contact: pawel.gazdzicki@dlr.de

Acknowledgements
This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No research 735969 (**INN-Balance**). This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme, Hydrogen Europe and Hydrogen Europe research.