



Optimization of the PBI membrane doping procedure

M. Paidar, A. Giurg, P. Mazúr, K. Bouzek
March 2014

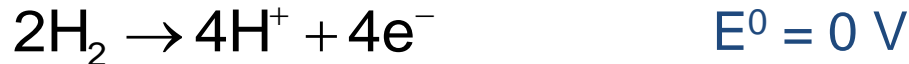
Institute of Chemical Technology Prague
Department of Inorganic Technology,
Technická 5, Prague 6, Czech Republic;



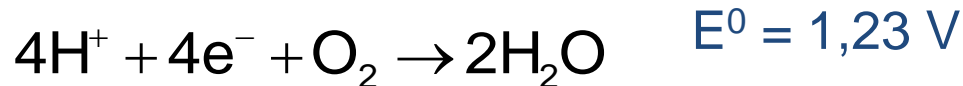


High Temperature PEMFC

anode



cathode



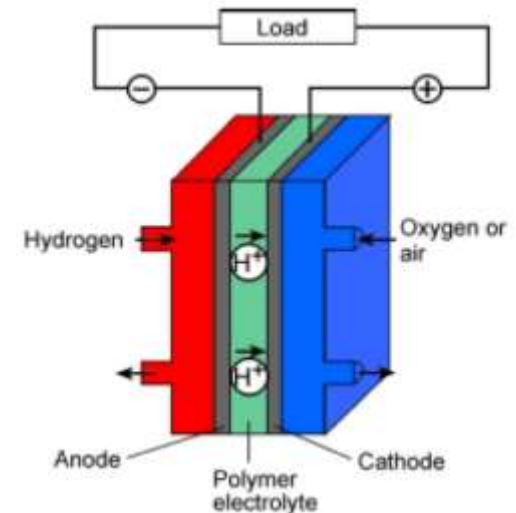
Main components

Membrane "solid electrolyte" permeable for H^+
PBI based polymers

Electrodes gas diffusion electrode with porous structure
platinum metals based catalyst

High temperature advantages

- simple water management
- limited CO poisoning
- electrode reactions kinetics enhancement

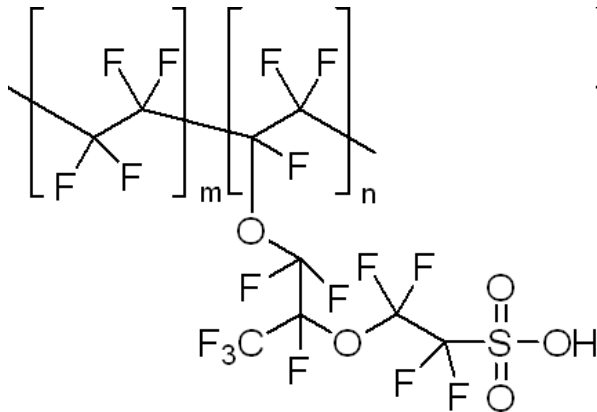




Polymer electrolyte membranes (PEM)

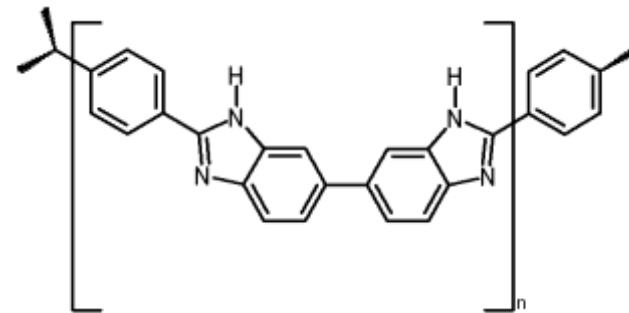
perfluorinated sulfonated-polymers (e.g. Nafion®)

- good chemical and mechanical stability
 - H^+ conductive (when swollen by liquid water)
- > losing H^+ conductivity above water boiling point!



polybenzimidazole (PBI) membranes

- impregnated by H_3PO_4
- > H^+ conductive up to 200 °C





Membrane doping procedure

- membrane cutting
- immersion to H_3PO_4
- doping time 2-8 h room temp.
- removing of H_3PO_4 droplets

Membranes:
PBI and APcl (crosslinked PBI)
by Fumatech (Germany)





Membrane conductivity

■ measuring temp. 160°C

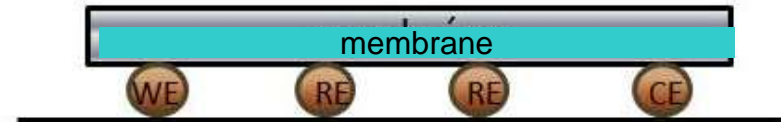
■ EIS 20Hz–20kHz

1. dry conditions

- 10 ml/min N₂

2. humidified conditions

- 10 ml/min N₂
- 0,6 ml/min H₂O (l) ~800ml/min (g)



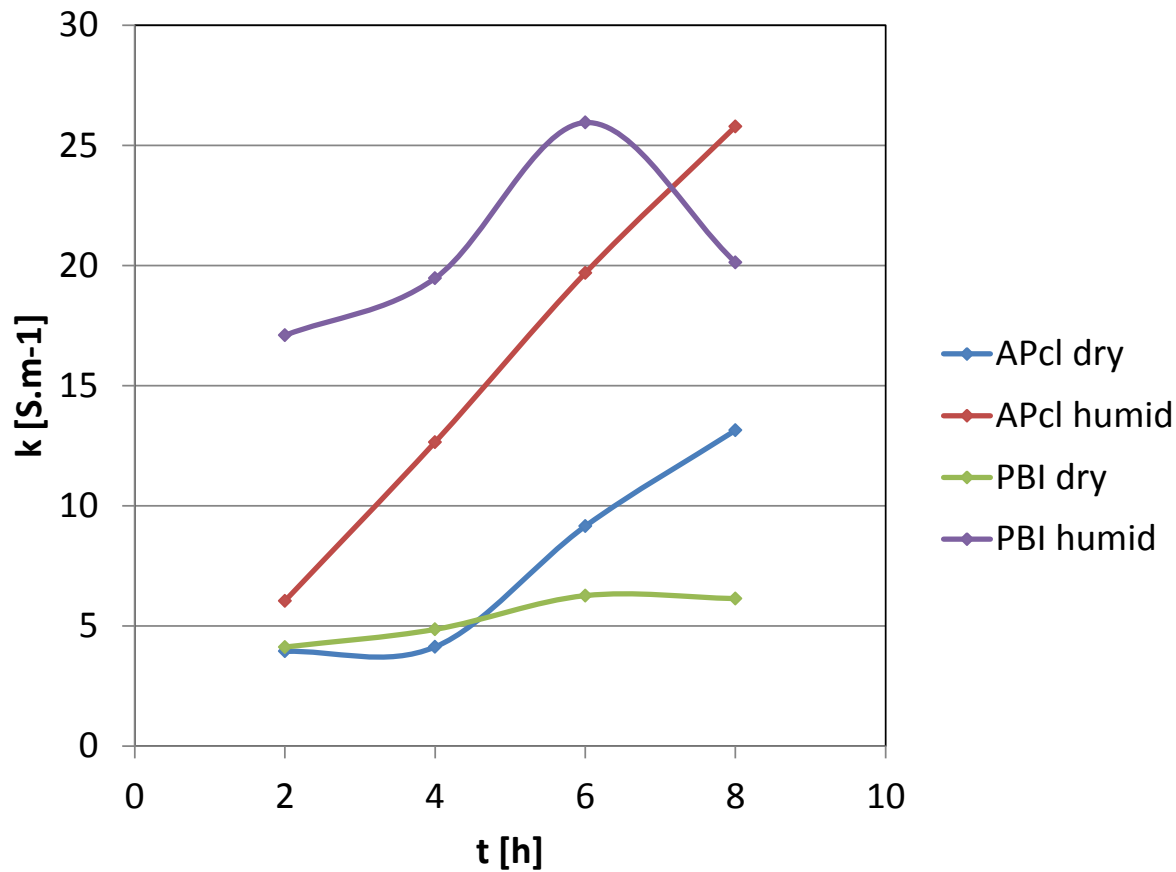
four electrode arrangement



conductivity cell



Membranes conductivity



t = 160°C

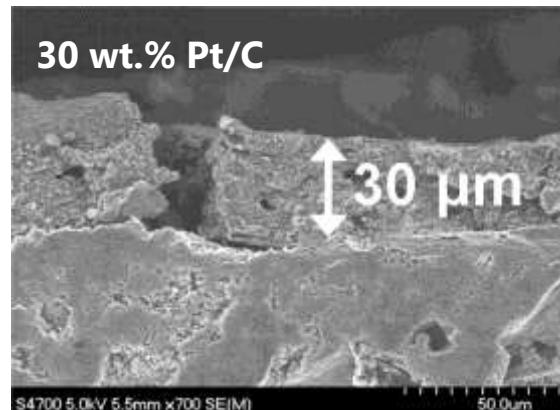


HT-PEM FC – set up

laboratory HT-PEMFC 6.25 cm²

- PBI based membranes
- 160 °C
- Cathode: O₂ / 20 ml min⁻¹
- Anode: H₂ / 30 ml min⁻¹

GDE – self production in laboratory

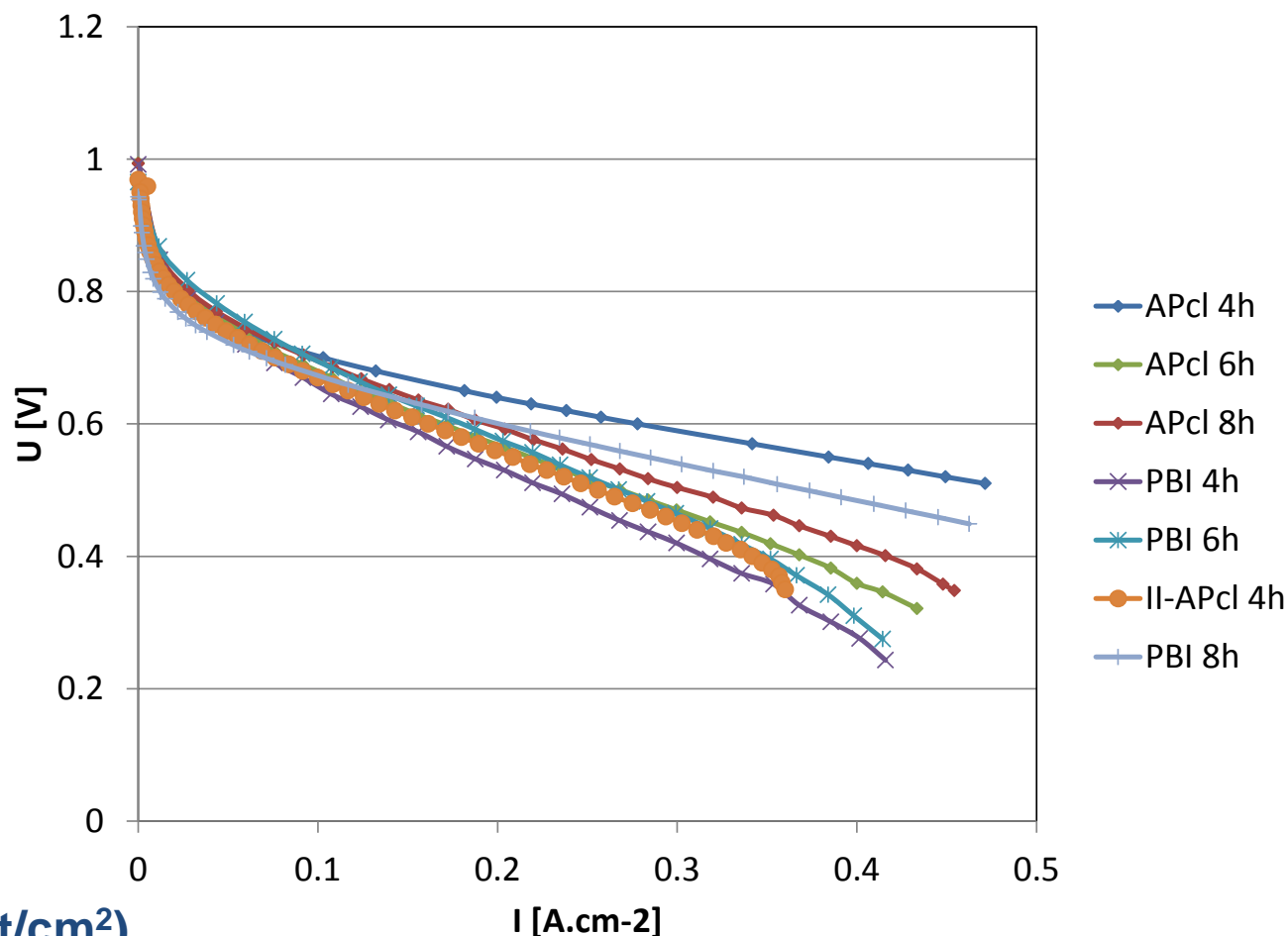


GDE ~0.5mg Pt/ cm²
XRD – Pt size 3.5 nm





PBI and APcl comparison



 H_2 / O_2

160 °C

GDE (~0.5 mg Pt/cm²)

100-200h conditioning period



optimized MEA

- Active area 6,25 cm²
- membrane PBI (Fumatech, GmbH) 6h
- Electrodes
 - cathode: 1,35 mg/cm² Pt
 - anode: 0,59 mg/cm² Pt



Durability test

■ Long term testing at constant load

- Operating temperature 160°C
- $\lambda = 1.2/2.0$ for H₂/air
- periodical electrochemical characterization: IV, EIS
- 1000 hours at 0.2 A/cm² constant load conditions

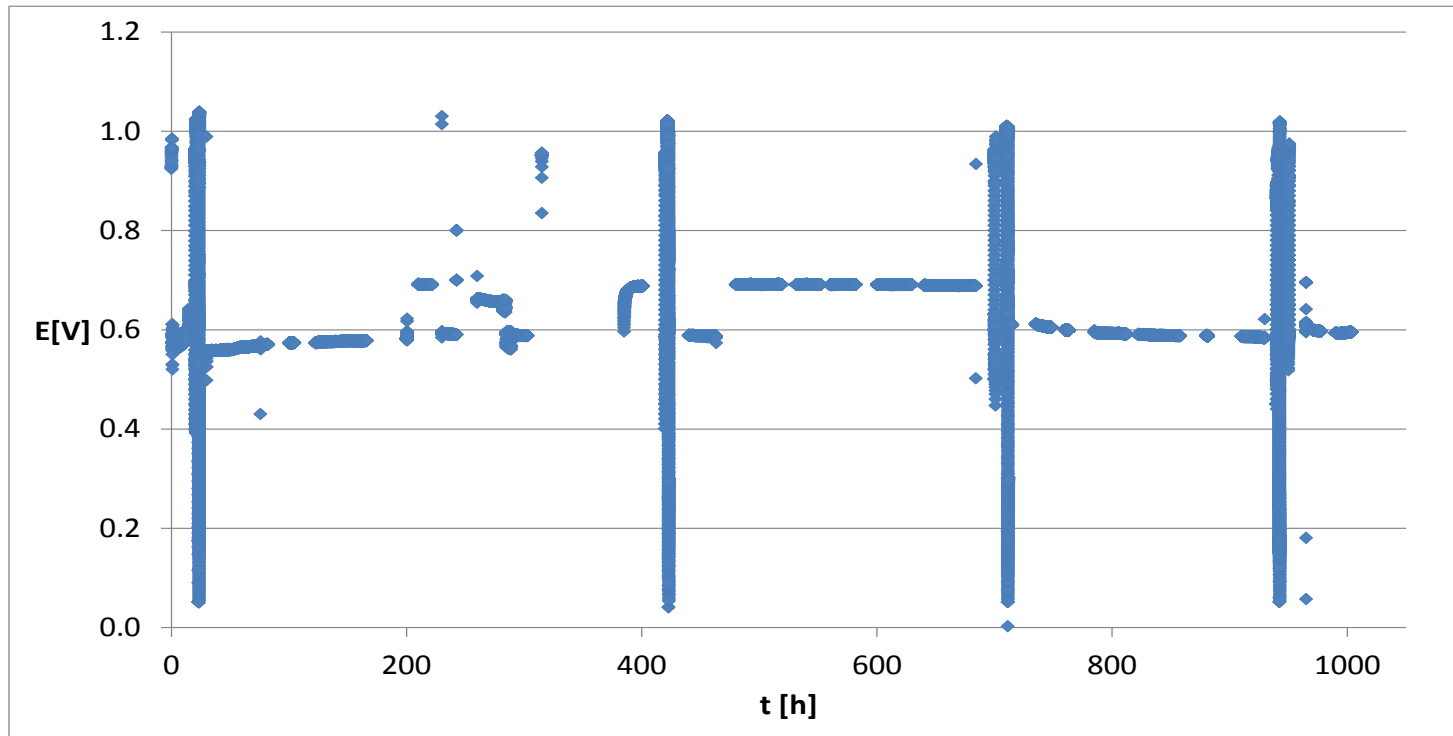


1000h test

Temperature 160°C

$H_2 / \text{air} = 1.2/2.0$

0.2 A/cm^2

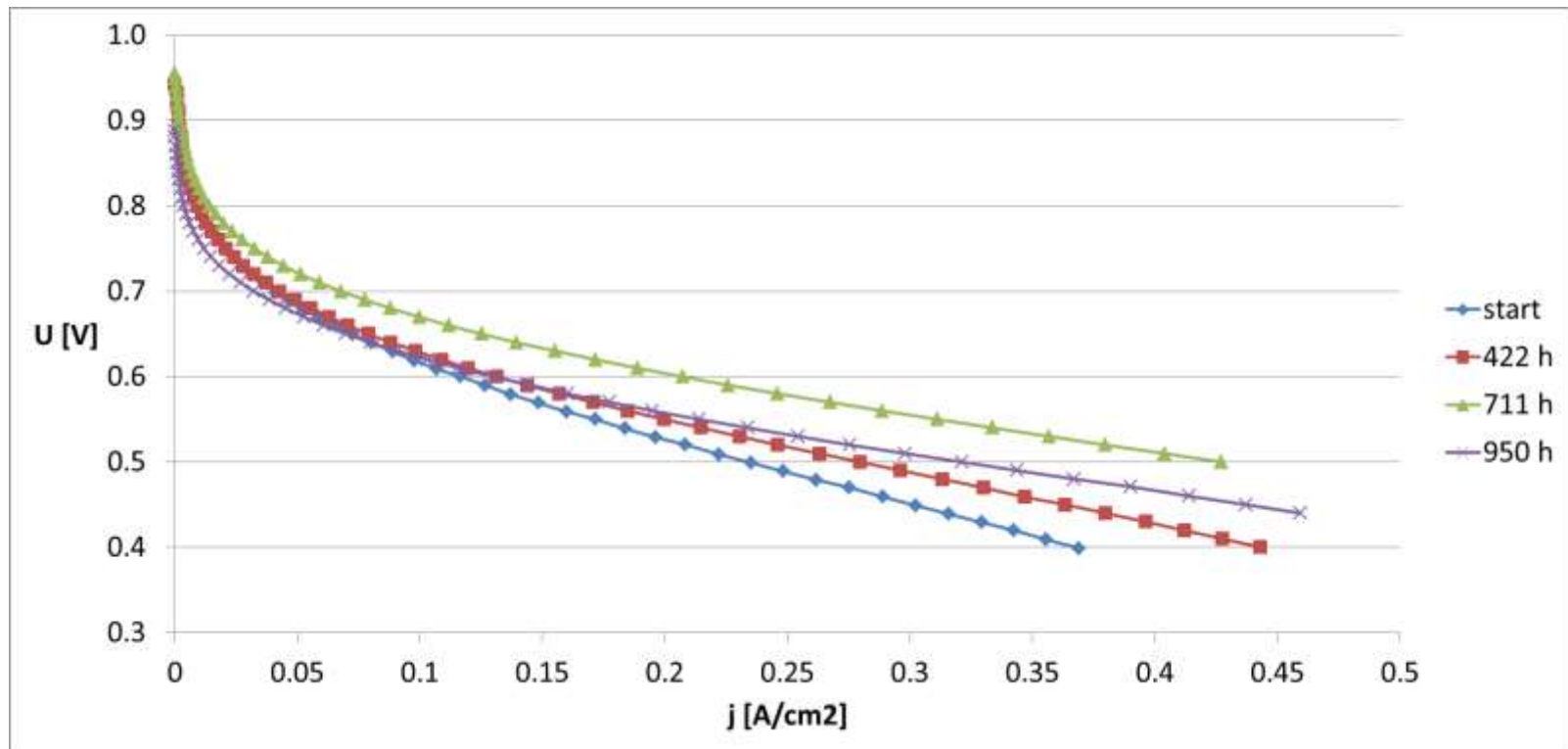




1000h test I-V curves

Temperature 160°C

$H_2 / \text{air} = 1.2/2.0$

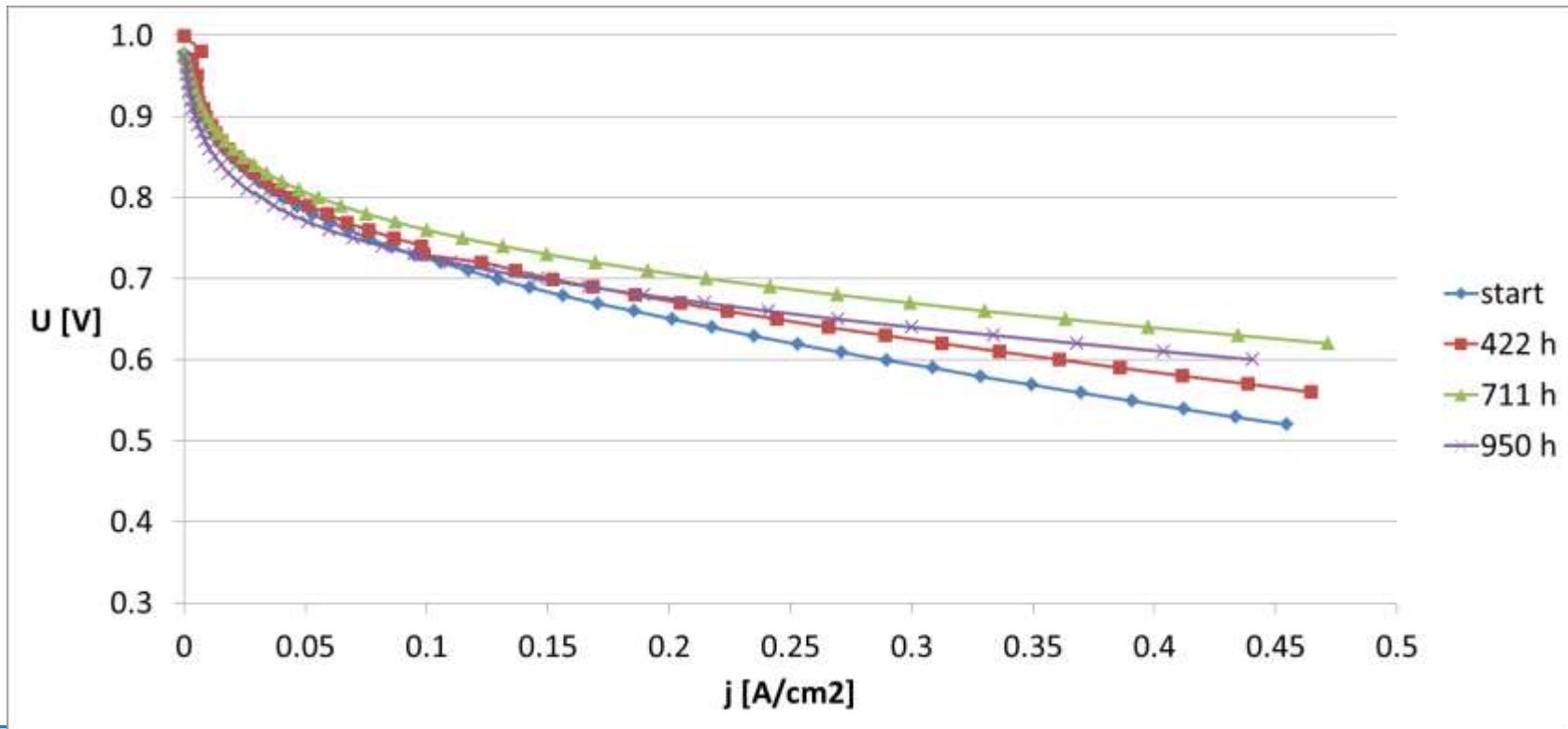




1000h test I-V curves

Temperature 160°C

$H_2 / O_2 = 1.2/2.0$

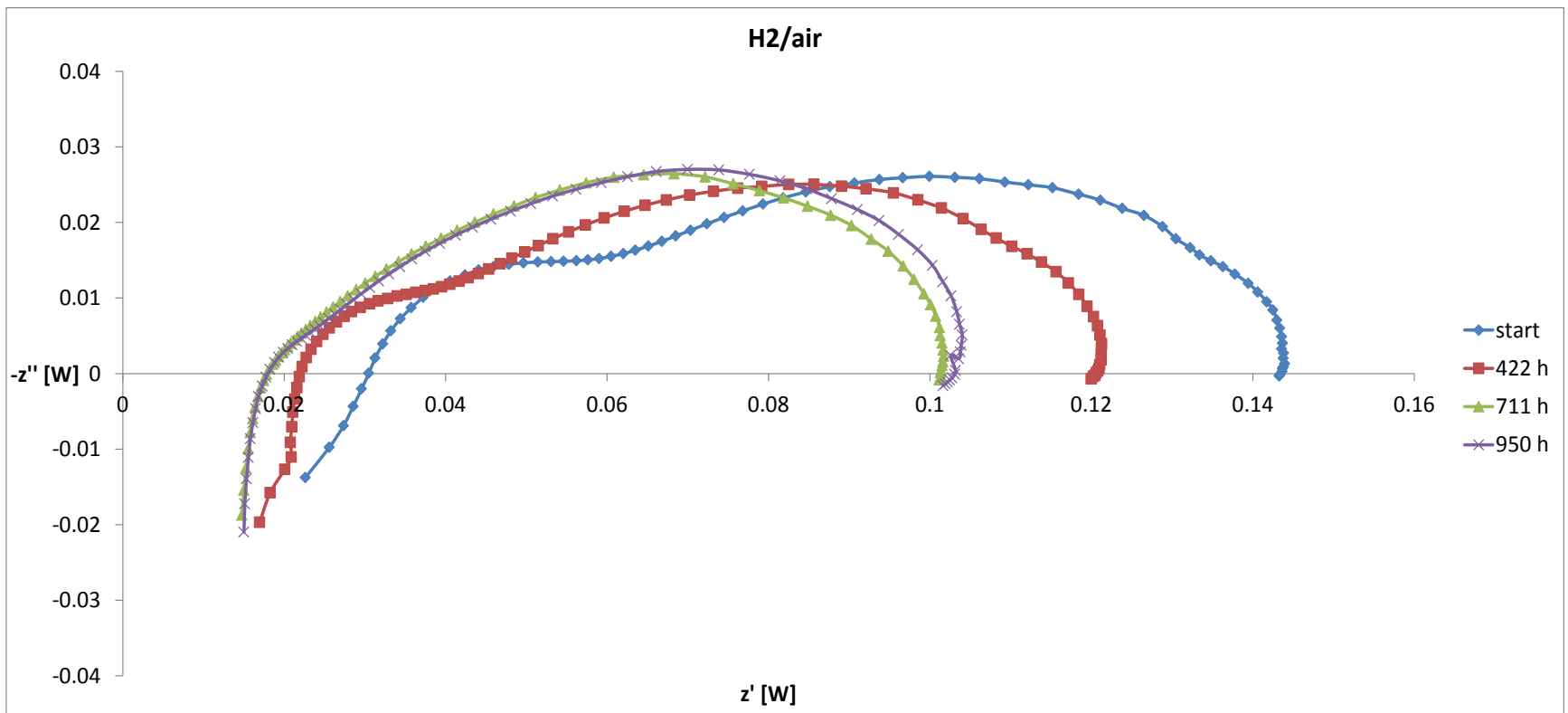




1000h test EIS

Temperature 160°C

$\text{H}_2 / \text{air} = 1.2/2.0$ at 0.2 A/cm^2





Conclusions

- crosslinking PBI causes slower membrane doping
- the conductivities of PBI membranes are more dependent on environment humidity than doping time
- HT-PEM MEA operated at 160 °C is able to operate without visible performance decrease over 1000h
- membrane conductivity improving during cell operation
- using oxygen rich gas – enhancement of performance



Thank you !

CISTEM project FCH JU within the framework of Contract No:325262
and by Ministry of Education, Youth and Sports of the Czech Republic
within the project No. 7HX13001