UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

Investigation of Pt Oxidation Kinetics at HT PEM Fuel Cell Conditions

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High temperature PEM fuel cells

Cell assembly and operation

- Similar to classical PEM
- Membrane - PBI impregnated by H_3PO_4
- 160°C - 180°C, fuel (H_2/syngas), oxidant (air/O_2)

Benefits

- Lower sensitivity to catalytic poisons
- Higher reaction rates
- More effective waste heat recovery

Fuel cell lifetime

- Crucial factor of commercialization

Components degradation

- Mostly irreversible
- Membrane (↑ ohmic losses, ↑ gases crossover)
- Catalyst layer (loss of EASA ≈ ↑ activation overvoltage)

Pt-C catalyst degradation

- Carbon support corrosion (loss of electric contact)
- Pt particle migration a coalescence (coarsening)
- Pt dissolution and re-deposition (mass loss, coarsening)

Pt dissolution mechanism

LT PEM FC

- Pt electrochemical dissolution (Pt^{2+}, Pt^{4+} ...)
- Pt oxides chemical leaching
- Pt oxides formation ($PtOH^{+}$, $PtOH$, PtO, PtO_2, PtO_4)

$$PtO + 2H^{+} + 2e^{-} \rightleftharpoons Pt + H_2O$$

HT PEM FC

- Young technology – degradation not primary problem
- Identical mechanisms but higher rates expected

Aims of this work

General

- Determine important mechanisms and kinetic parameters of Pt-C catalyst degradation in HT PEM FC
- Develop mathematical modeling tools enabling prediction of HT PEM FC life time

Objectives of this presentation

- Pt oxide formation/reduction mechanism by:
  - Linear sweep cyclic voltammetry
  - Mathematical modeling of reaction kinetics

Experimental setup

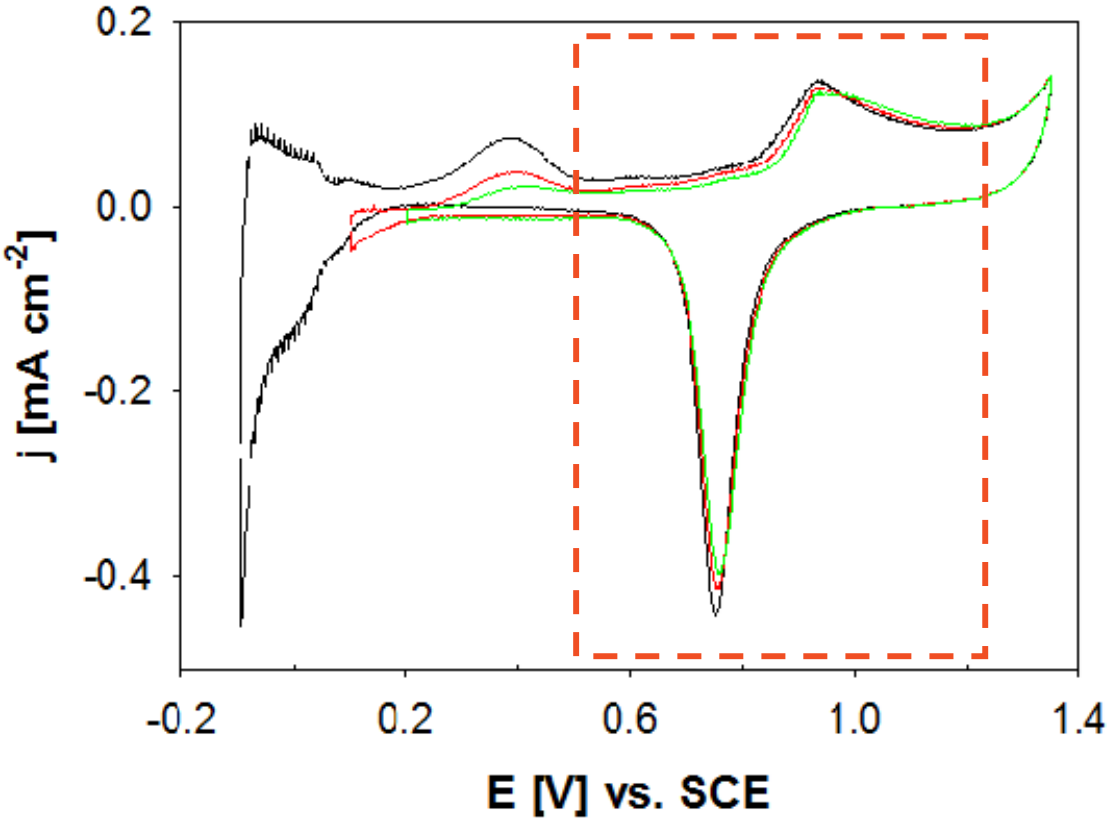
Experimental cell

- Electrolyte – 99.6% H_3PO_4, t = 42 °C to 160 °C
- Deaerated (O_2 less conditions)
- Three-electrode arrangement:
  - WE and CE: Pt sheets (polycrystalline, area 1 cm^2)
  - RE: SCE (25 °C, connected via double salt bridge)

Cyclic voltammetry conditions

- Sweep rate (E_{rate}) of 0.05 - 0.50 V s^{-1}
- Cathodic vertex potential E_c = 0.51 V [SCE]
- Anodic vertex potential E_a = 0.85 – 1.4 V [SCE]

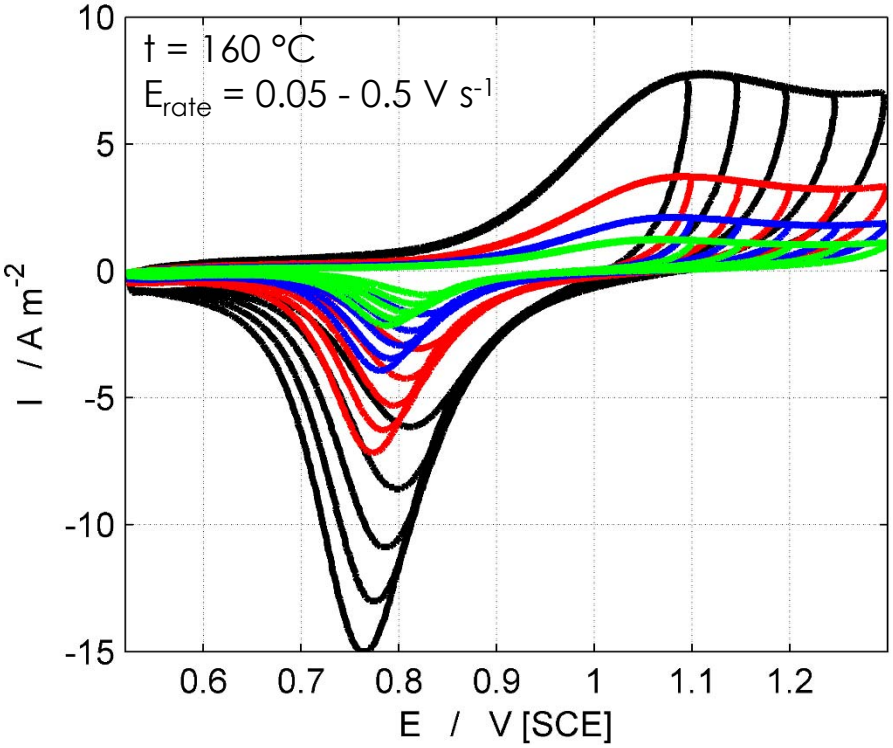
Typical CV scan



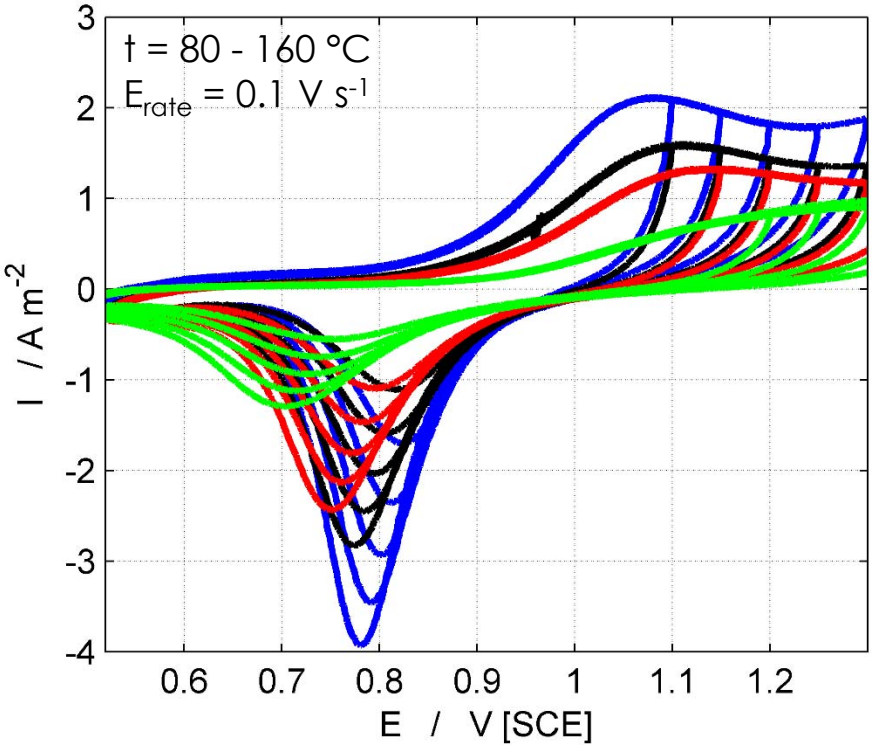
CV conditions: E_{rate} = 0.050 V s^{-1}, t = 160 °C, E_c = -0.1 - 0.2 V [SCE], E_a = 1.35 V [SCE]

Typical CV scan

Potential sweep rate



Temperature



Kinetic model

Kinetic equation

$$r = \boldsymbol{k_a}\left(1 - \frac{\theta_{PtO}}{2}\right)\exp\left(-\frac{\boldsymbol{\omega_a}}{RT}\theta_{PtO}\right)\exp\left\{+\frac{\boldsymbol{\alpha_a}F}{RT}(E - \boldsymbol{E_r})\right\} -$$

$$-\boldsymbol{k_c}\left(\quad + \frac{\theta_{PtO}}{2}\right)\exp\left(-\frac{\boldsymbol{\omega_c}}{RT}\theta_{PtO}\right)\exp\left\{-\frac{\boldsymbol{\alpha_c}F}{RT}(E - \boldsymbol{E_r})\right\}$$

PtO mass balance

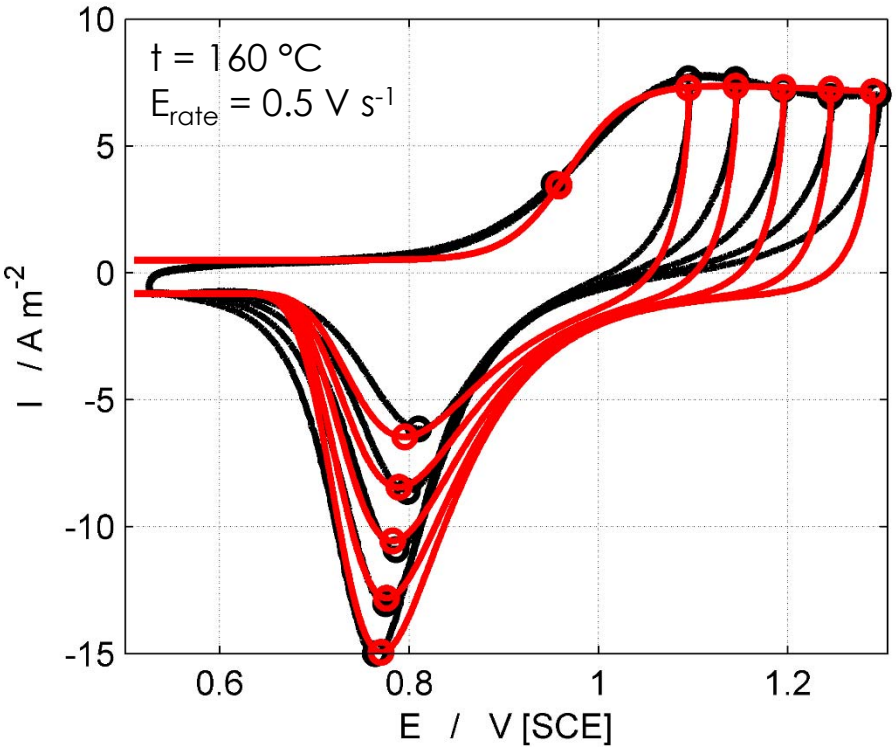
$$\frac{\partial\theta_{PtO}}{\partial t} = -\frac{r}{\Gamma_{Pt}}$$

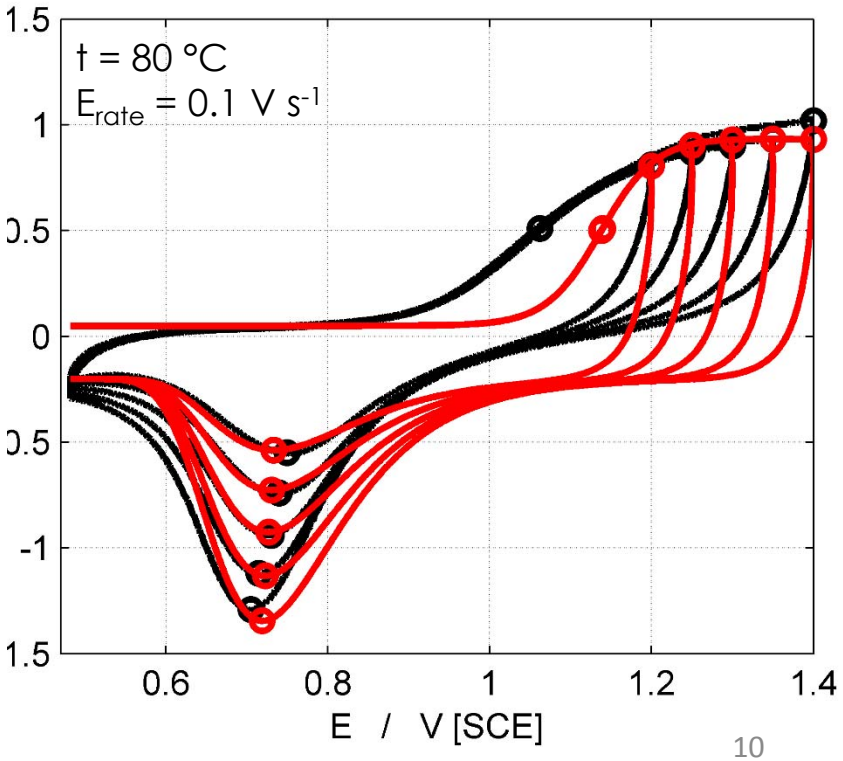
- Finite element method
- Implemented in COMSOL
- 7 parameters fit

Kinetic model

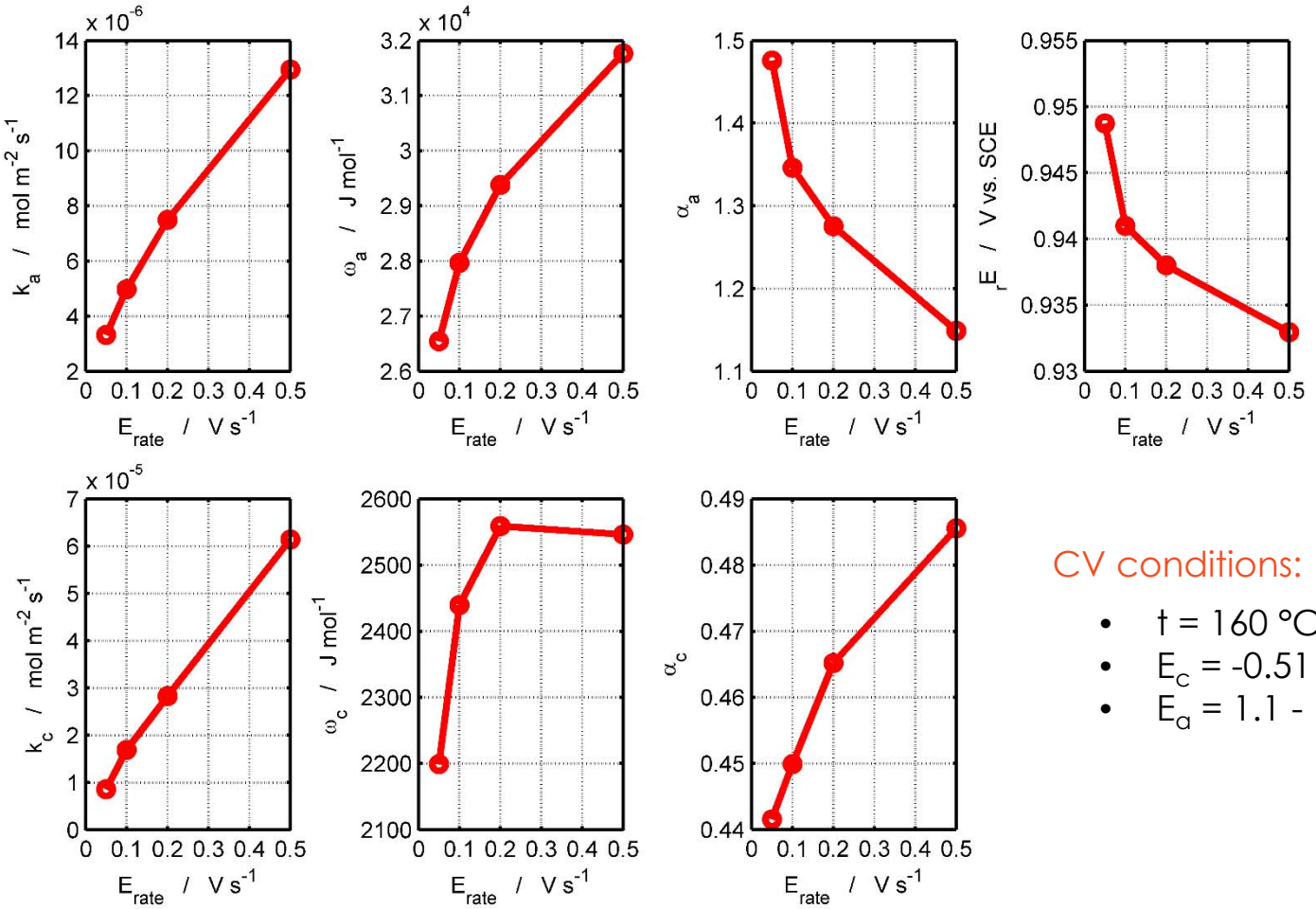
Optimization procedure

- Optimization algorithm (Matlab, "*fminsearch*" function)





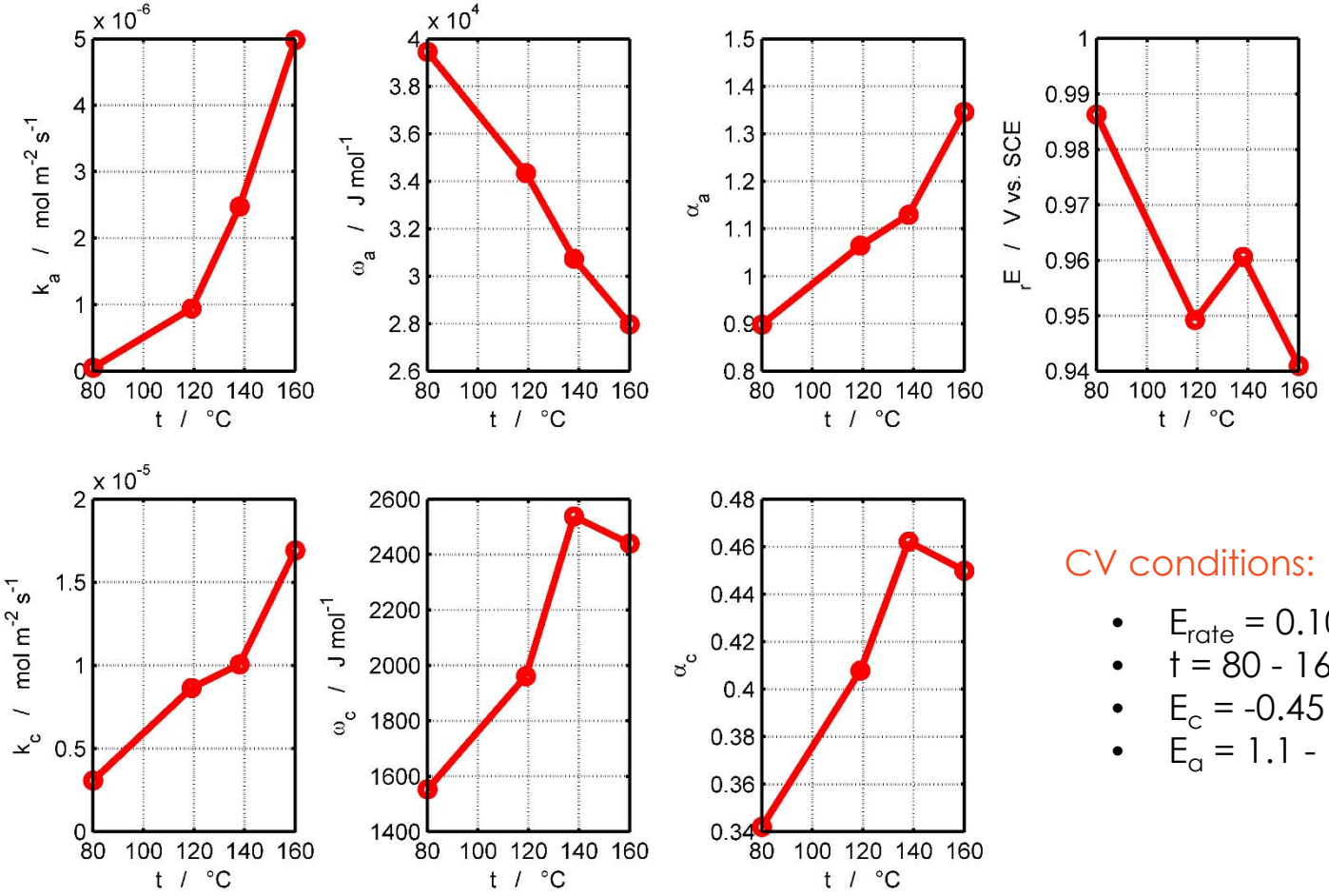
Effect of potential sweep rate



CV conditions:

- t = 160 °C
- E_c = -0.51 V [SCE]
- E_a = 1.1 - 1.3 V [SCE]

Effect of temperature



CV conditions:

- E_{rate} = 0.10 V s^{-1},
- t = 80 - 160 °C
- E_c = -0.45 V [SCE]
- E_a = 1.1 - 1.4 V [SCE]

Summary

Main conclusions

- Mechanism of Pt-oxides formation is complex and seems similar to that under LT PEM FC conditions
- ↑ Temperature ≈ ↑ reaction rates
- Pt surface passivation at E > 1.05 V [SCE]

Future prospects

- More thorough analysis of parameter optimization
- Elucidation of observed trends
- Moving from Pt-sheet to real GDE with Pt nanoparticles
- Etc…

Thank you for your attentions