Degradation of Pt Catalyst in High Temperature PEM Fuel Cell

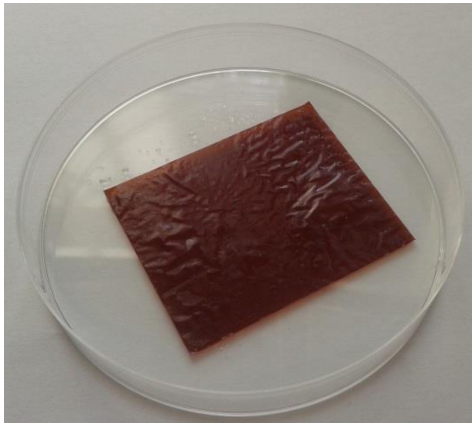
T. Bystron, M. Prokop, K. Bouzek

New Energy World JU
fuel cells & hydrogen for sustainability

ICT PRAGUE

High temperature PEM fuel cell

- Operating temperature 150 -200 °C
- Medium resistance to catalyst poisoning
- Combined heat & power systems
- Often based on H_3PO_4 doped polybenzimidazole (PBI) membranes
- H_3PO_4 at elevated temperature is very aggressive media
- Degradation of gas diffusion electrode (GDE)

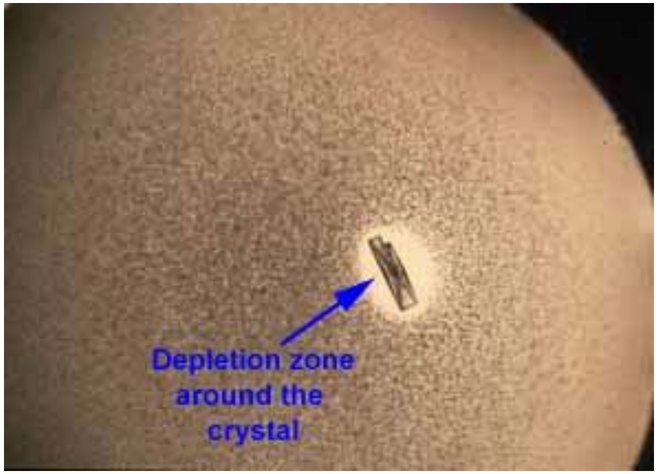


PBI membrane doped with H_3PO_4

GDE degradation mechanisms

- Mechanical damage – loss of electric contact to catalyst layer
- Chemical or electrochemical oxidation of carbon support
- Catalyst poisoning
- Agglomeration & sintering
- Pt corrosion
- Electrochemical Pt dissolution

} Ostwald ripening



*Disappearance of small crystals around large one due to Ostwald ripening **

*http://xray.bmc.uu.se/terese/tutorial6.html

Pt dissolution

$Pt_{(s)} \leftrightharpoons Pt^{2+}_{(aq)} + 2\ e^-$ **$E^0 = 1.188\ V$**

$Pt_{(s)} + H_2O \leftrightharpoons PtO_{(s)} + 2H^+ + 2\ e^-$ **$E^0 = 0.980\ V$**

$PtO_{(s)} + 2\ H^+ \leftrightharpoons Pt^{2+}_{(aq)} + H_2O$

Activity, concentration of H^+ and H_2O in 95% H_3PO_4 at 160 °C ??

$PtO_{(s)} + H_2O \leftrightharpoons PtO_{2(s)} + 2H^+ + 2\ e^-$ **$E^0 = 1.045\ V$**

$PtO_{2(s)} + 4\ H^+ \leftrightharpoons Pt^{4+}_{(aq)} + 2\ H_2O$

$PtO_{2(s)} + 4\ H^+ + 2\ e^- \leftrightharpoons Pt^{2+}_{(aq)} + 2\ H_2O$ **$E^0 = 0.837\ V$**

Well established for low temperature PEM fuel cell conditions!

Pt in hot concentrated H_3PO_4

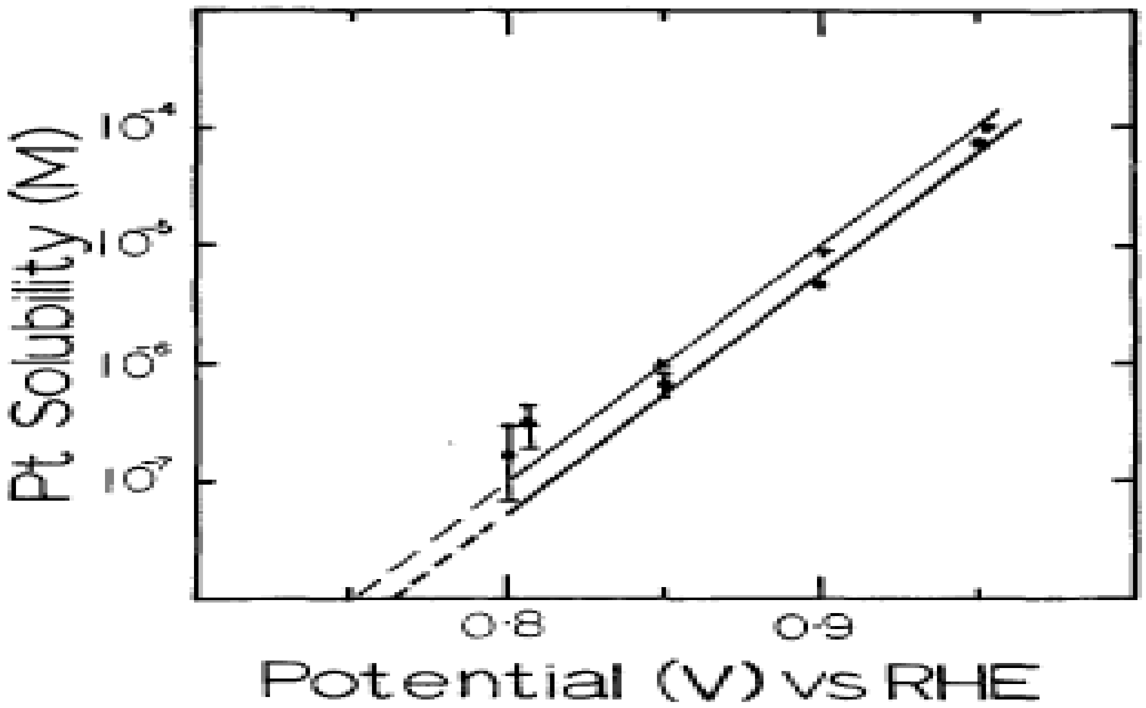


Fig. 1. Potential dependence of platinum concentration in 96% H_3PO_4 at 176°C (●) and 196°C (▲).

<u>Pt^{2+} present in the solution</u>

P. Bindra, S.J. Clouser, e. Yeager, J. Electrochem Soc. 126 (1979), p.1631.

Usual FC testing operation

- Break-in procedure
- Constant current (voltage) operation
- EIS measurements at various conditions (Ohmic resistance, polarisation resistance)
- Cyclic (linear) sweep voltammetry (Performance/loading curve)
- Post-mortem analysis
- Complex system + complex operational conditions -> difficulties to distinguish indiviual degradation effects
- Trade-off: number of information while loosing control vs. limitted inumber of information while keepin high level of control

Aim of the work

- Simple constant voltage (potential) HT PEM FC degradation tests

- Find link between FC operational conditions and Pt crystallite size

Experimental - HT PEM FC

GDE:

- Home made GDEs (Pt loading approx. 0.5 mg cm^{-2})
- HiSPEC4000 catalyst (40 % Pt/Vulcan C) + 10 % PTFE + Sigracet GDL 34 BC

FC testing:

- 30 ml min^{-1} H_2, 20 ml min^{-1} O_2, no gas preheating, no humidification
- Active area of 6.25 cm^2 , 160 °C
- 2-3 PBI membranes (6 hour doping in 85 % H_3PO_4)

  (separation after dismantling, Pt crystallite size determination)
- Constant voltage mode

EIS:

- 2-electrode arrangement, potentiostatic mode, 100 kHz – 1 Hz, amplitude 10 mV

X-ray diffraction

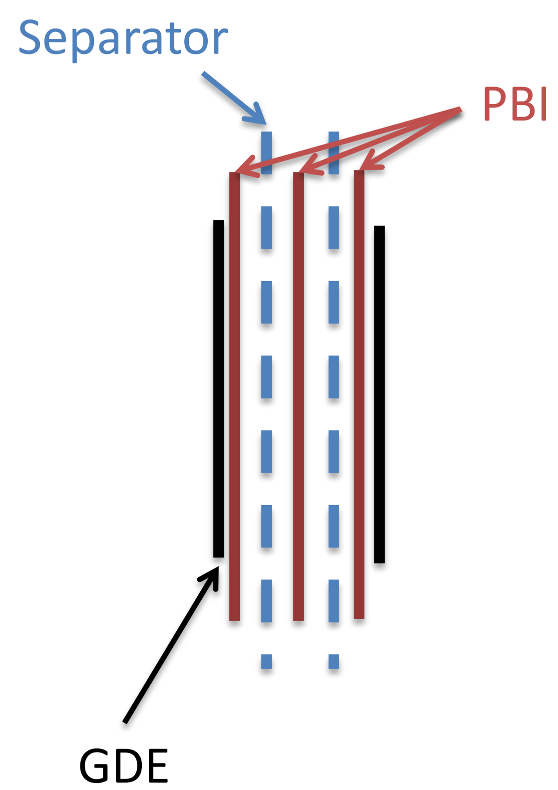
- Average crystallite size

PBI membrane separator

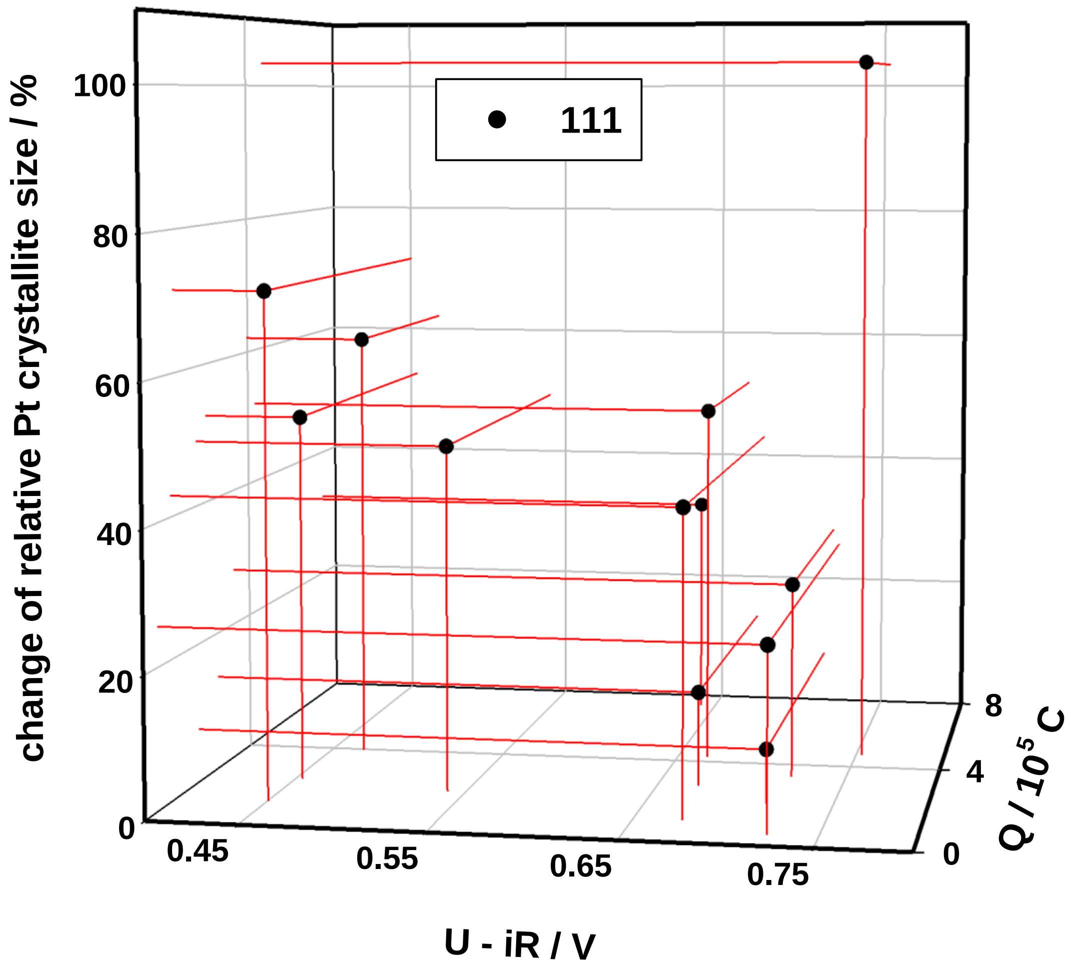
Enabling separate analysis of anode and cathode after FC operation

- *Pt crystallite size*
- *Pt mass*

- Separator



Pt crystallite size - cathode



Pt crystallite size change as function of FC voltage and charge

Surface phenomena

$$E_{eq} - E^{0'} = \frac{RT}{nF} ln \frac{a_{Pt2+}}{a_{Pt}} - \frac{3V_m \sigma_{surf}}{nF} \frac{1}{r}$$

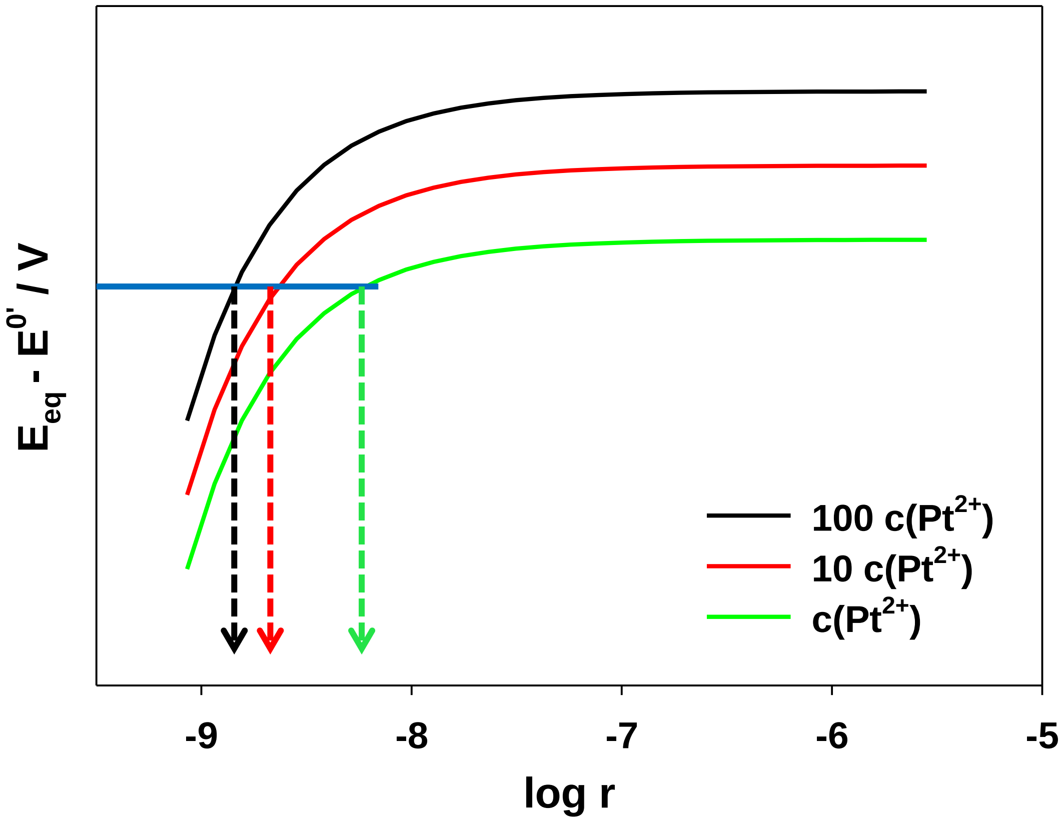
$Pt_{(s)} \leftrightharpoons Pt^{2+}{}_{(aq)} + 2\ e^-$

$E_{eq} - E^{0'}$ - Overpotential

V_m - Pt molar volume

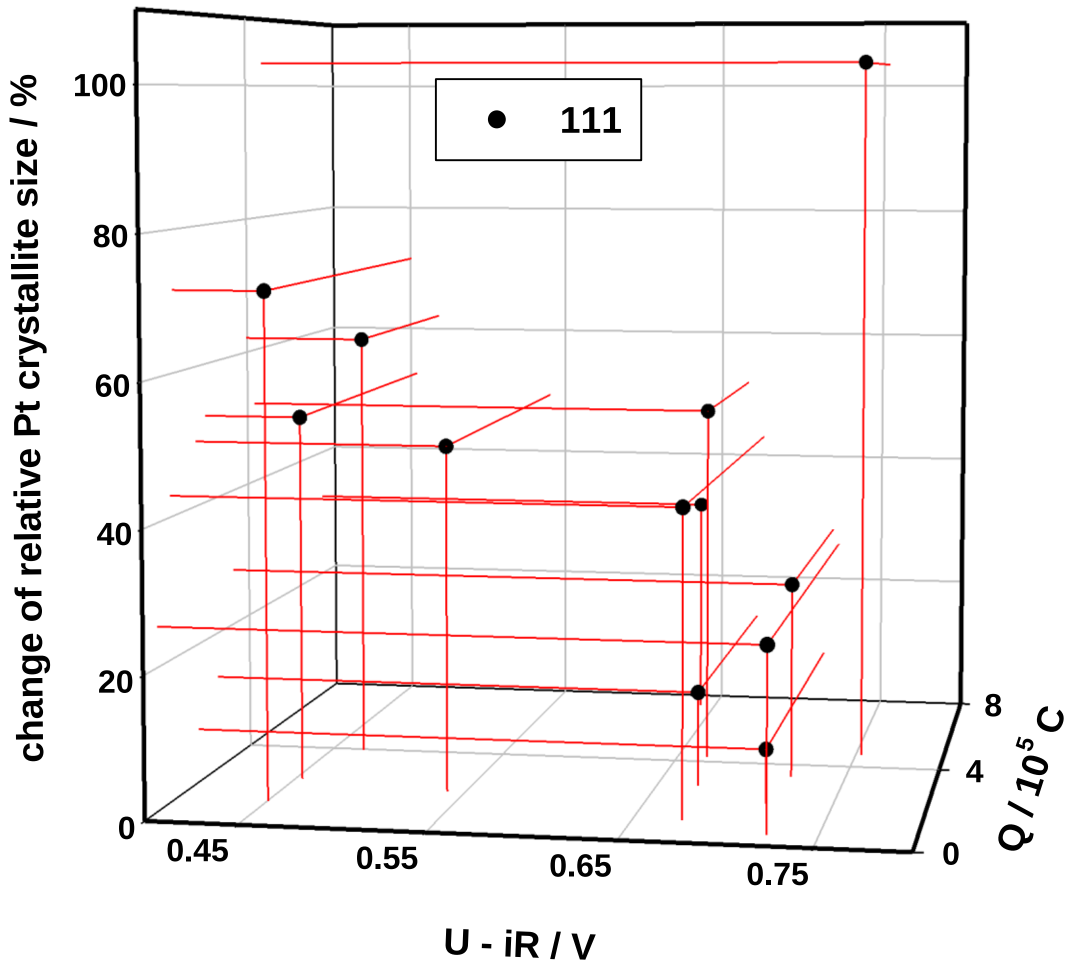
σ_{surf} - Pt surface energy

r - Pt particle radius



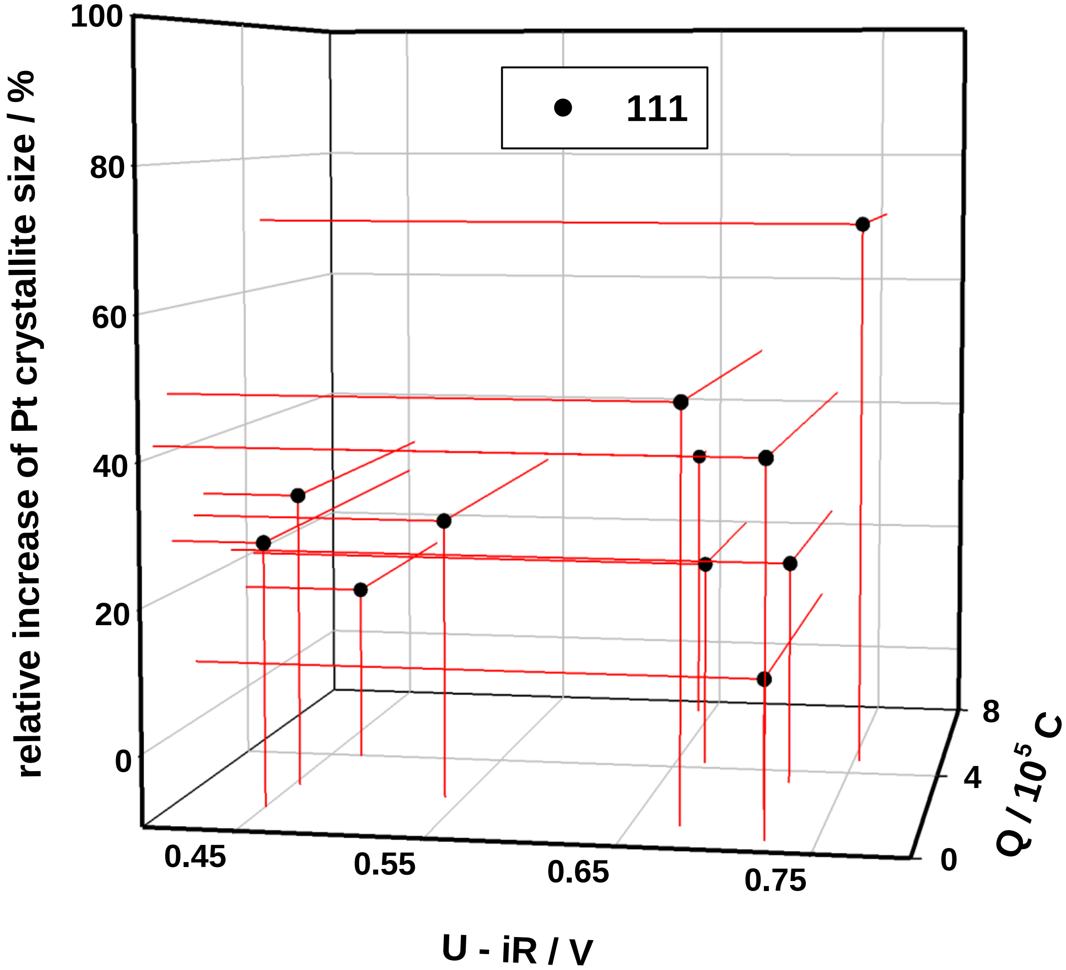
More pronounced degradation expected at higher electrode potential / cell voltage at constant σ_{surf}

Pt crystallite size - cathode



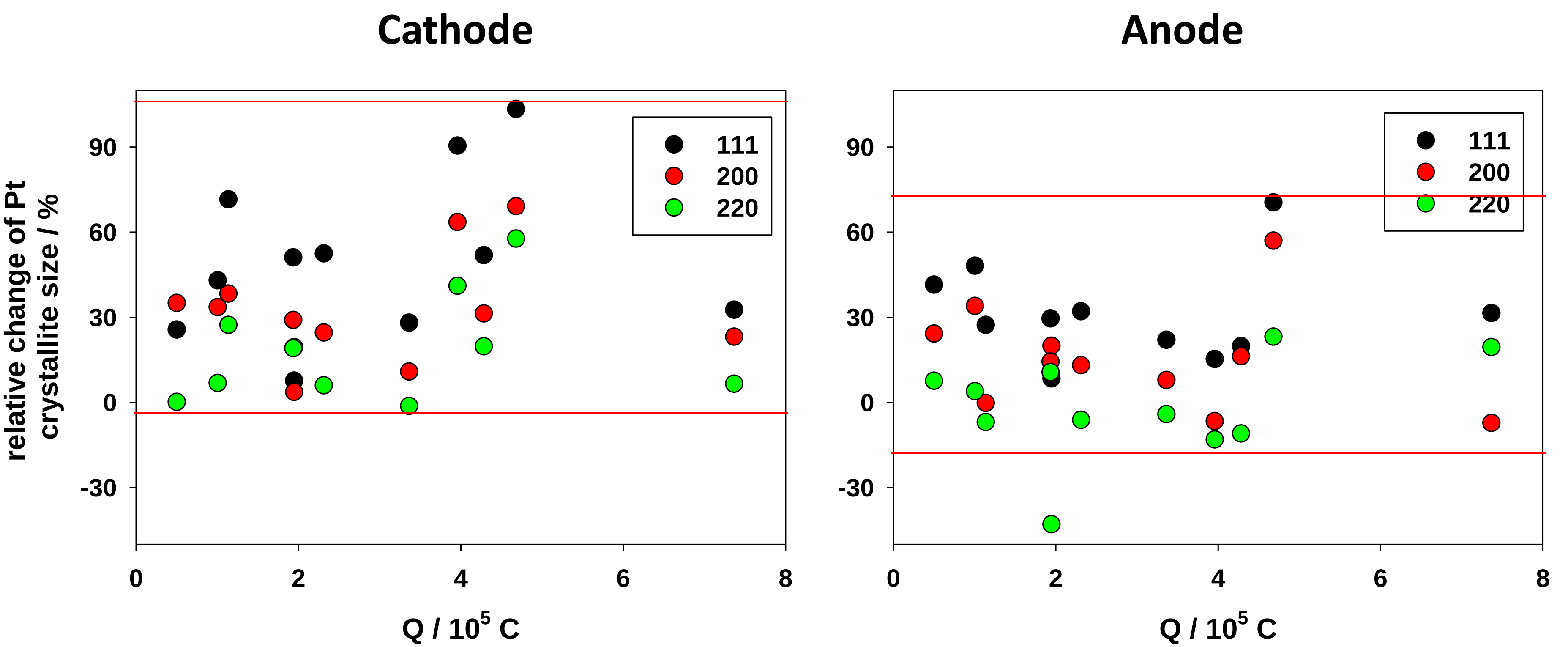
Pt crystallite size change as function of FC voltage and charge

Pt crystallite size - anode



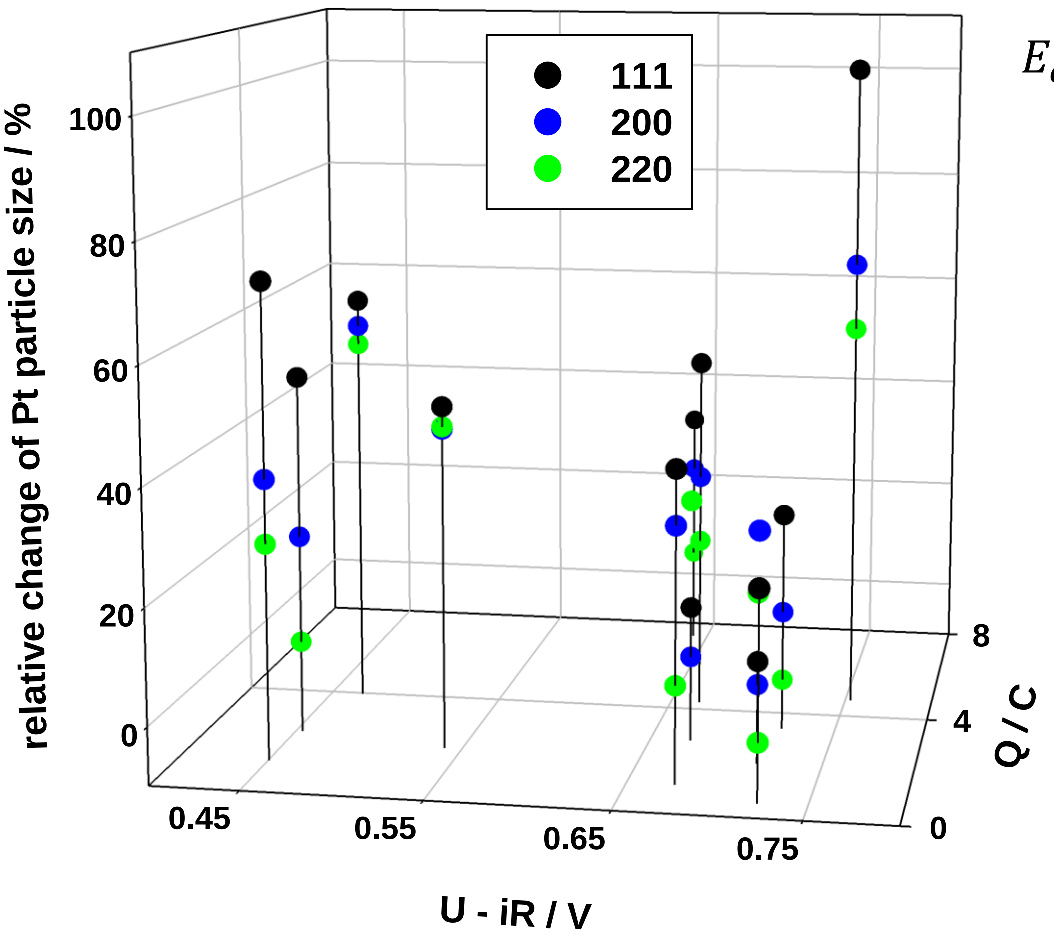
Pt crystallite change as function of FC voltage and charge

Pt crystallite size – cathode vs. anode



Pt crystallite diameter change as function of charge

Pt crystallite size - cathode, different hkl planes



$$E_{eq} - E^{0'} = \frac{RT}{nF} ln \frac{a_{Pt2+}}{a_{Pt}} - \frac{3V_m \sigma_{surf}}{nF} \frac{1}{r}$$

$$- \frac{V_m}{VnF} \sum_{hkl} A_{hkl}\, \sigma_{hkl,surf}$$

Pt crystallite size change as function of FC voltage and charge

Summary

- Simple constant voltage FC experiments
- Pt crystallite growth more pronounced on the cathode
- Faster cathode Pt crystallite size growth at lower FC voltage (lower potential)
- Surface energy dependent on the electrode potential?
- Potential independent growth of Pt crystallites on the anode
- Crystallite growth sensitive on the surface orientation (surface energy)

Thank you