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Electrocatalytic activity and stability of antimony doped tin oxide supported platinum catalyst for PEM fuel cells

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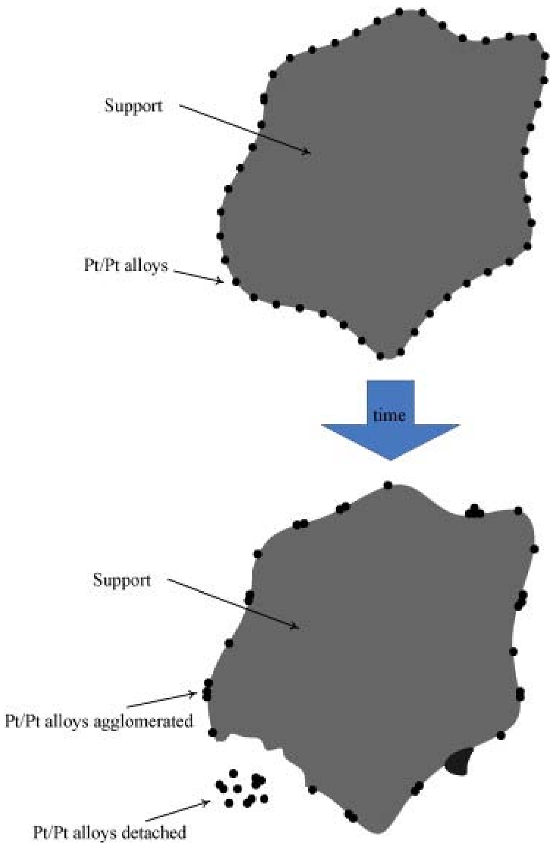
Introduction

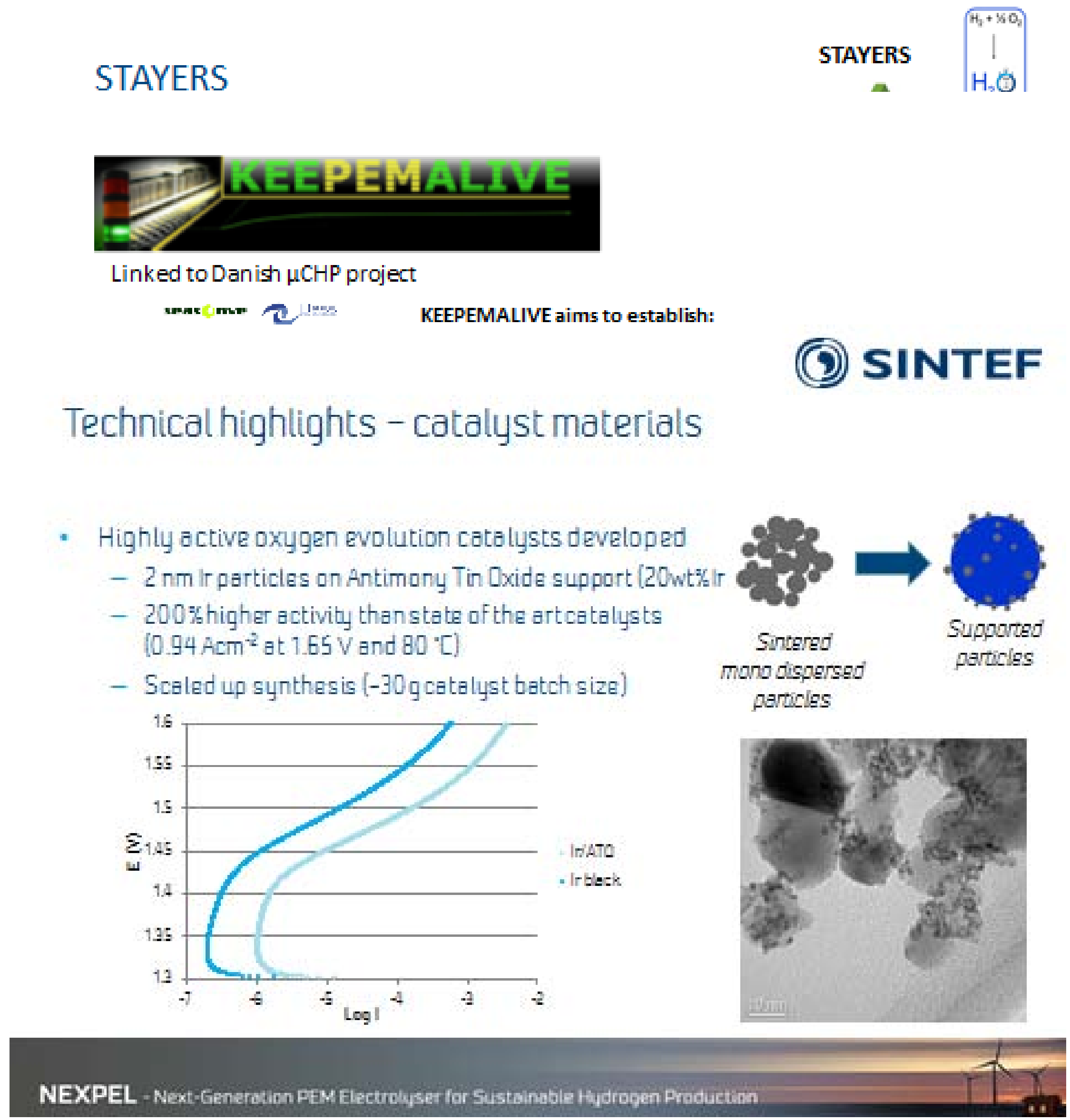
- Catalyst degradation is one of the main causes of reduction of PEM fuel cell performance
- Loss of catalyst active surface area
  - Sintering, dissolution/precipitation
- Corrosion of catalyst support
  - Loss of catalyst/support contact
  - Changes in surface chemistry
  - Collapse of catalyst layer
  - Reduction in conductivity/connectivity of electronic pathways.



Yuyan Shao, Geping Yin, Yunzhi Gao
Journal of Power Sources Volume 171, Issue 2 2007 558 - 566

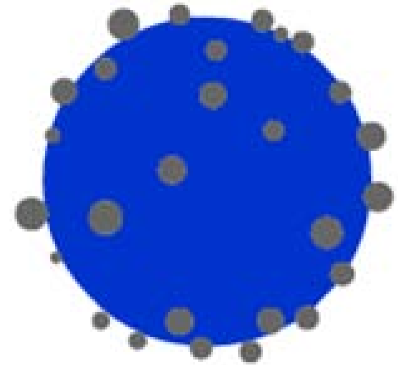
Background

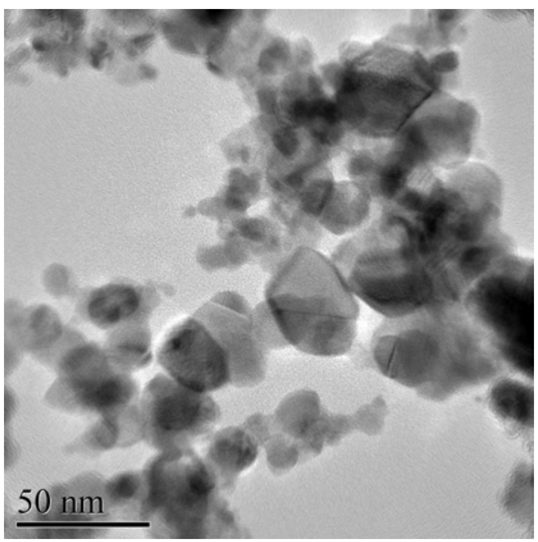
- Several FCH-JU projects on PEM fuel cell degradation
- High competence on synthesis of complex oxides
- Previously developed a highly active Ir/ATO catalyst for PEM electrolysers.
- Initial trials for development of oxide supported Pt catalysts



Targeted catalyst composition and morphology

- Platinum nanoparticles (d ~ 2-4 nm)
- Antimony doped Tin Oxide as support
- Platinum loading of 20 wt%
- Polyol method selected for synthesis
  - Gives small particle size and narrow size distribution

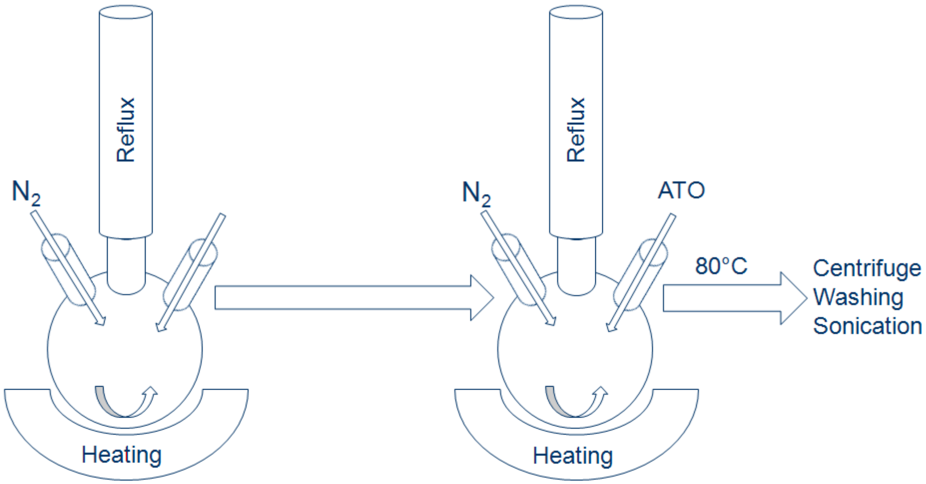




BET surface area : 37 m^2g^{-1}
Particle size: 10-50 nm
Doping level: 7-11 % Sb
High stability in acidic media and at elevated potentials
Relatively high electronic conductivity (> 10^{-3} S cm^{-1})

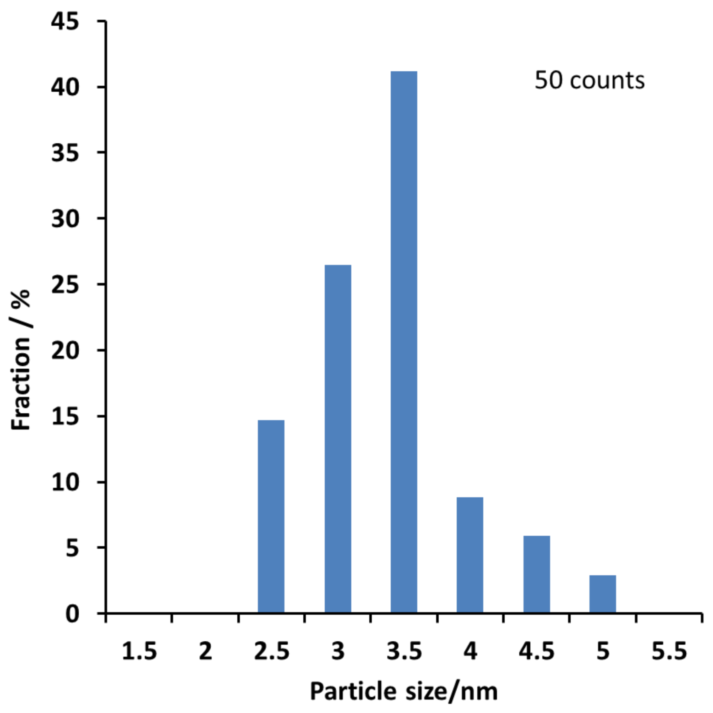
Experimental – Synthesis (Polyol Method)

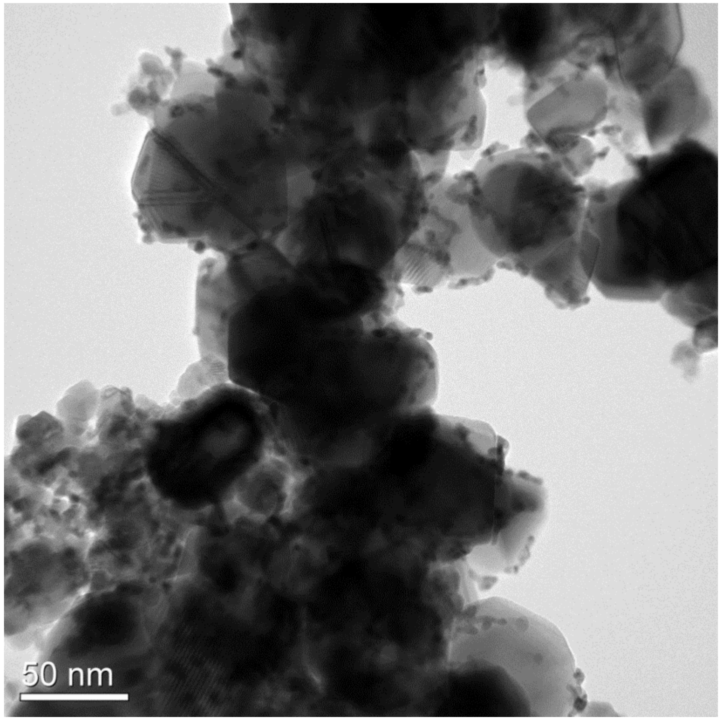
1. **Isolate Platinum**
   Reflux Pt-precursor
   pH adjusted EG solution
   high temperature
2. **Add support**
   Antimony Tin Oxide
   well dispersed
   reflux lower temperature
   Adjust pH
3. **Isolate catalyst**
   Centrifuge to remove EG
   Sonicate and rinse until pH is that of rinsing water



TEM analysis

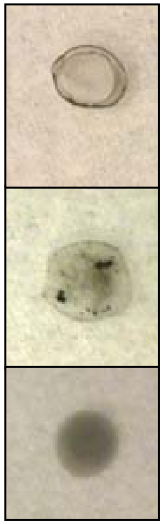
- Average particle size 3.2 nm
- Well dispersed on ATO surface





Thin-film Working Electrode Preparation

1. Aqueous catalyst suspension (1 mg_{CAT} / ml)

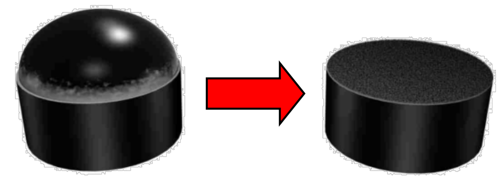


Only Milli-Q water (pH 7)

50/50 Water/iso-propanol (pH 5-6)

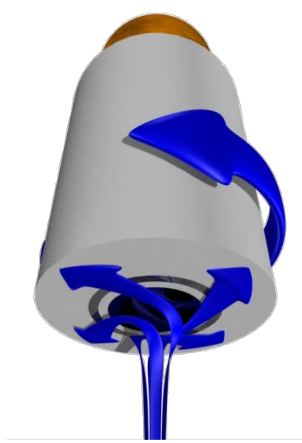
Milli-Q water at pH 3

2. Thin-film electrode



1. 20 μl of catalyst suspension
2. Dry under Ar atmosphere
3. 20 μl of 0.05 wt.% Nafion
4. Dry under Ar atmosphere

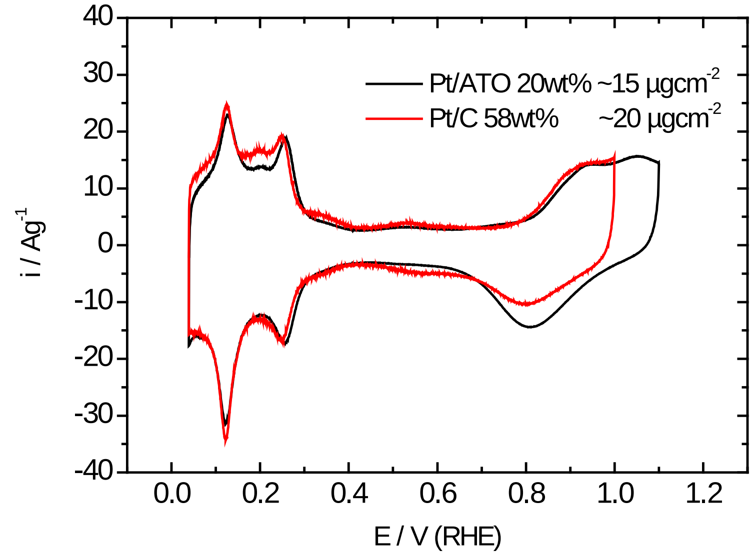
<u>Catalyst deposited = 20 ± 3(7%) μg</u>

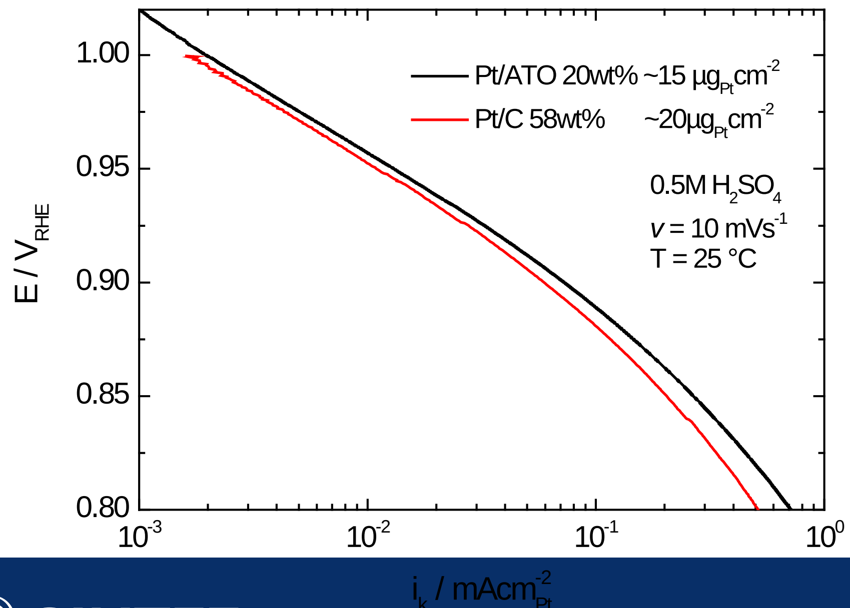


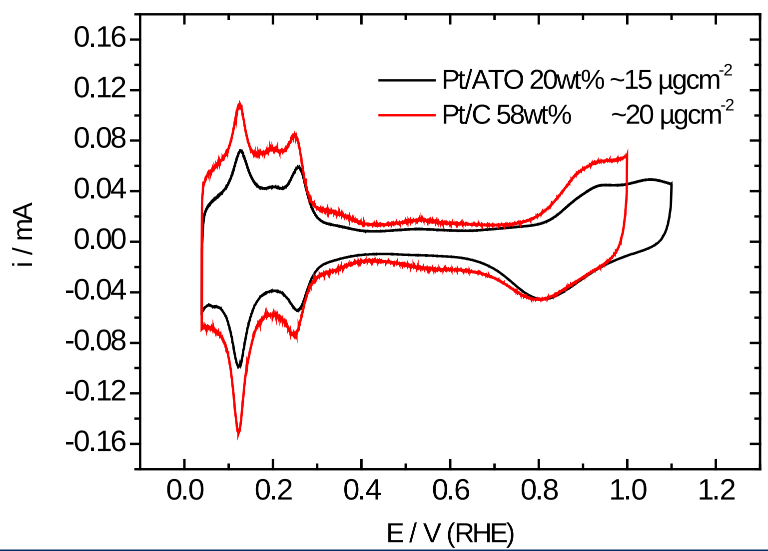
3. Rotating Disk Electrode
(Pine Instrument) is used
for performing the
electrochemical measurements
in 0.5 M H_2SO_4 electrolyte
geometric area: 0.196 cm^2

Pt/ATO vs Pt/C

- Comparison of fresh catalyst with commercial 58wt% Pt/C
  - 15µg 20wt% Pt/ATO & 20µg 58 wt% Pt/C gives roughly same electrode thickness
  - ECSA and catalytic activity very similar (107 & 106 cm^2g^{-1})

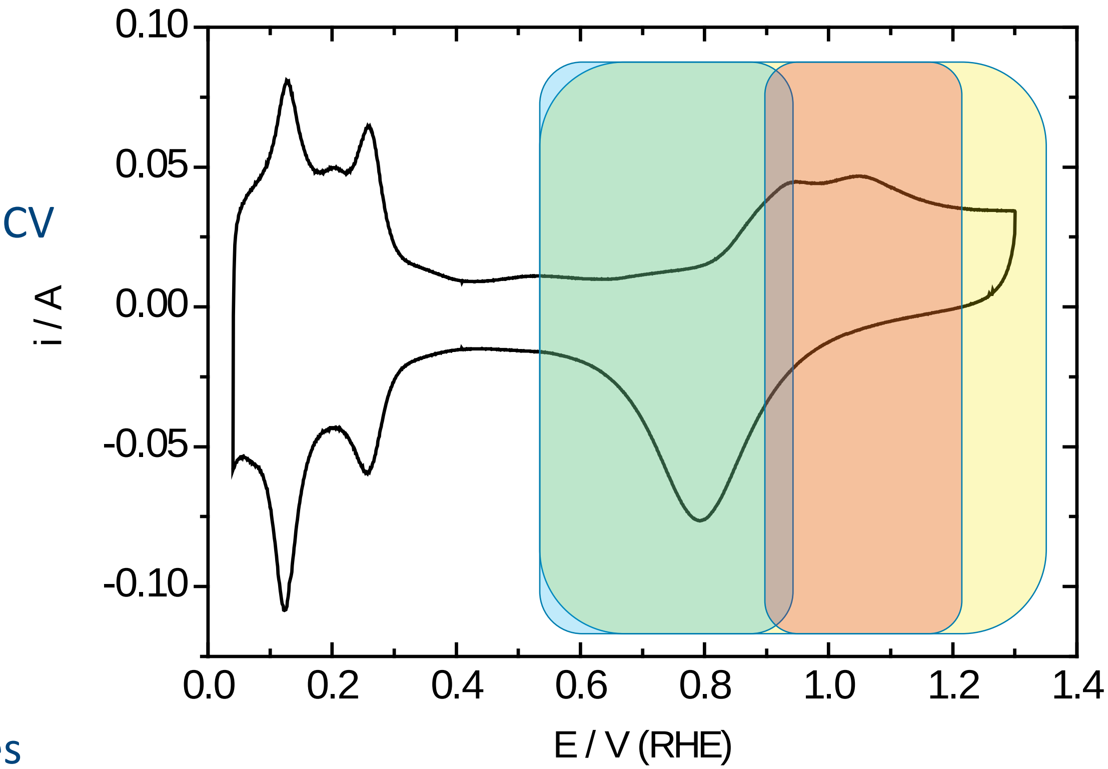






AST Protocols

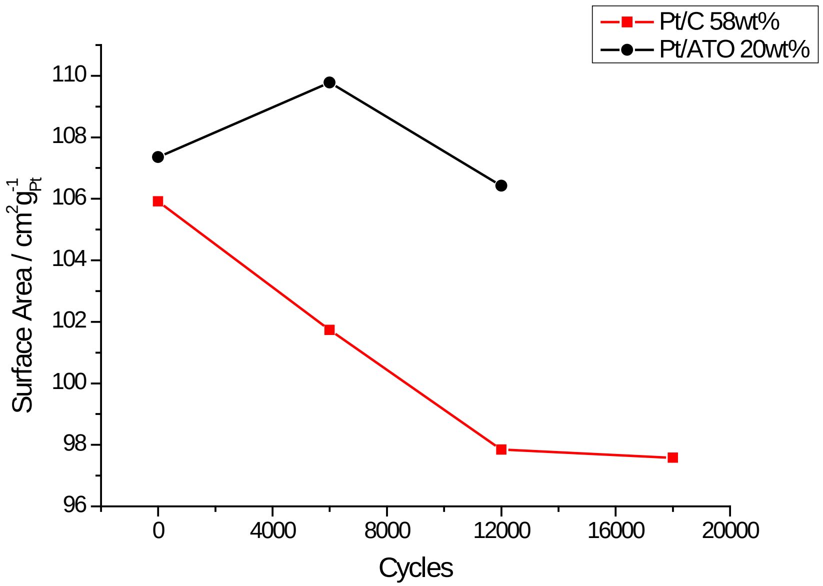
- Catalyst stability evaluated against three different AST protocols
- Load cycling (0.55-0.95V):
  - Mimic normal FC operation.
  - Pt catalyst in reduced state
- Start up(0.9-1.2V):
  - Elevated potentials due to OCV and gas purge
  - Catalyst in oxidized state
- Shut down (0.55-1.35V)
  - Elevated potentials due to gas purge
  - Catalyst cycled between reduced and oxidised state
  - Elevated carbon corrosion rates

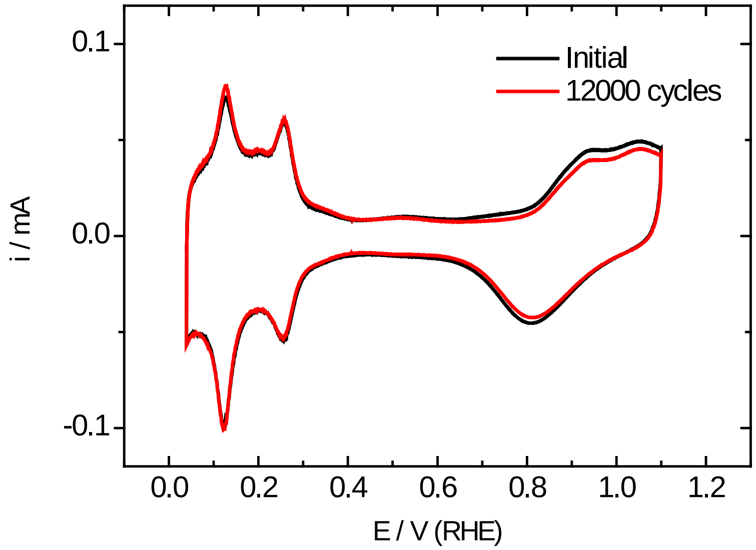


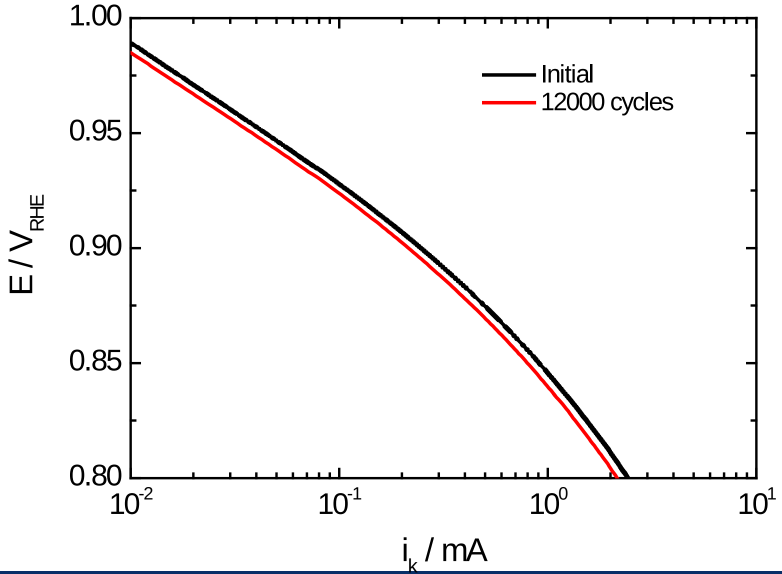
Results - Load cycling

0.55V-0.95V
800 mVs^{-1}
12000/18000 cycles

- Pt/ATO show no change in ECSA or ORR activity
- Pt/C ECSA reduced by 8%



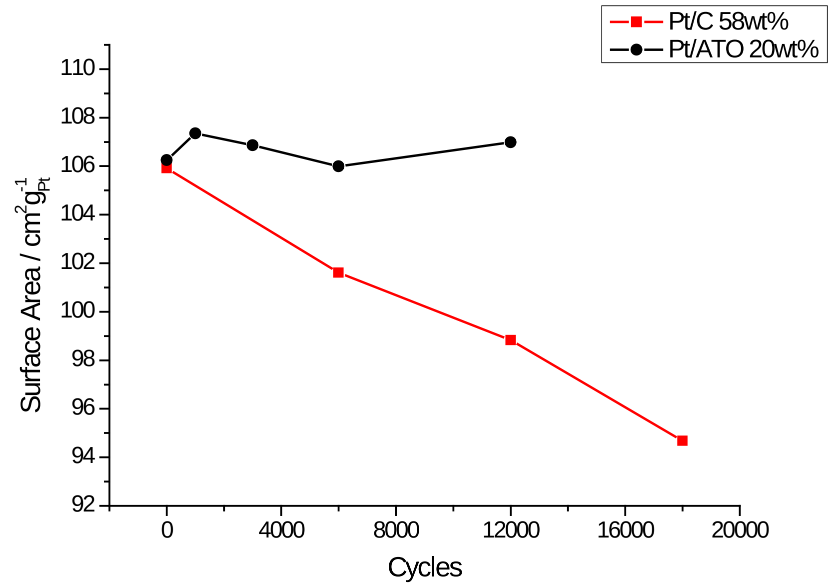


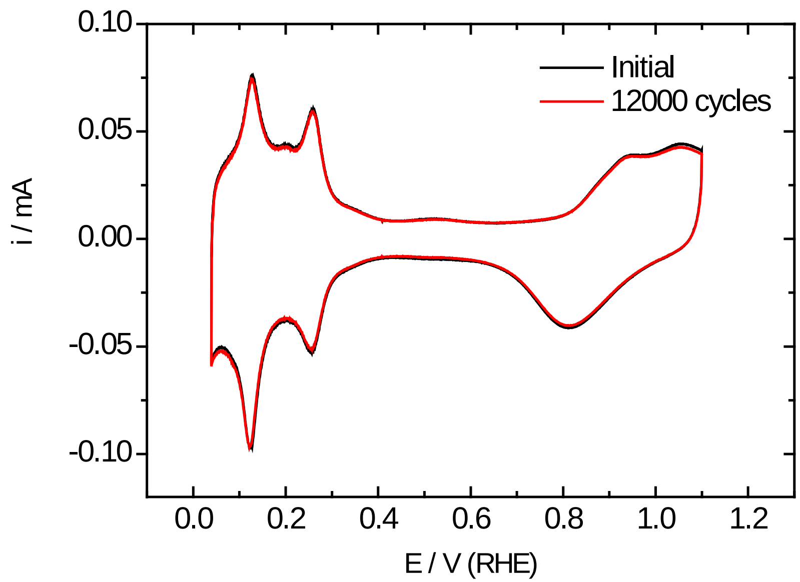


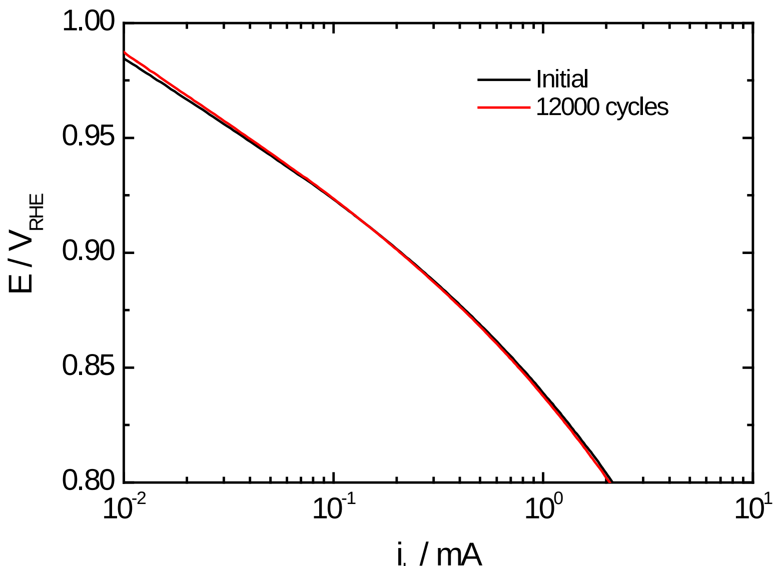
Results - Start Up

0.9V-1.2V
800 mVs^{-1}
12000/18000 cycles

- Pt/ATO show no change in ECSA or ORR activity
- Pt/C ECSA reduced by 12%



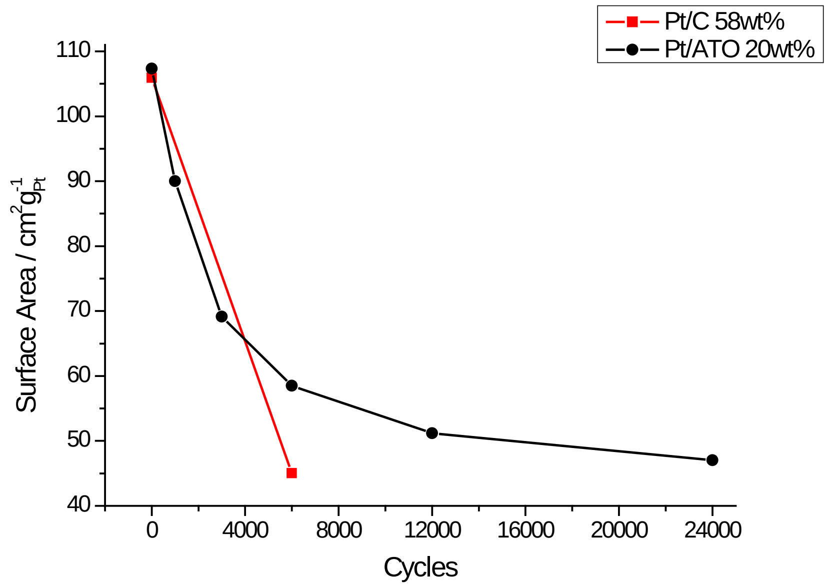


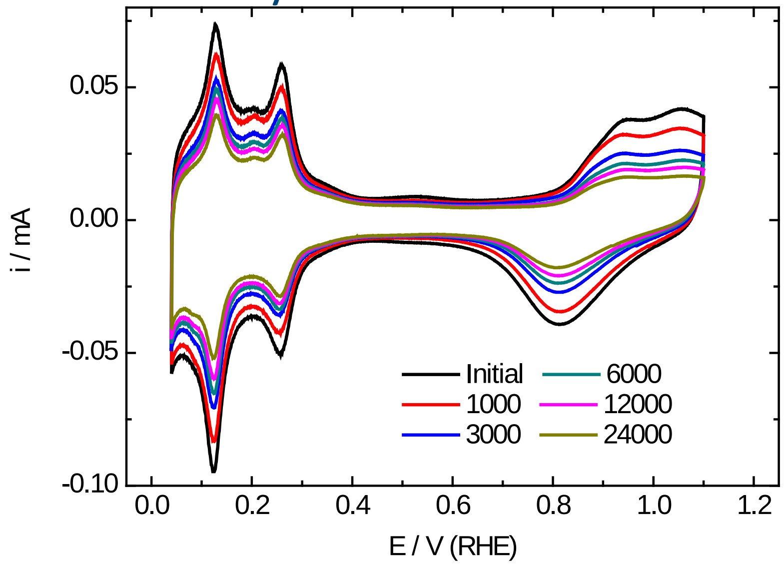


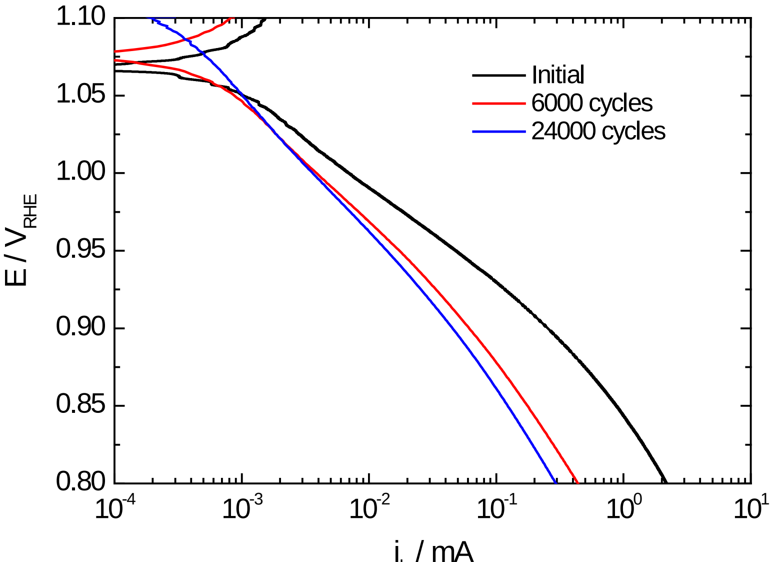
Results - Shut Down

0.55-1.35 (Pt/ATO)
0.6-1.2V (Pt/C)
800 mVs^{-1}
24000/5000 cycles

- Pt/ATO ECSA reduced by 55% after 24000 cycles
- Pt/C ECSA reduced by 60% after 5000 cycles

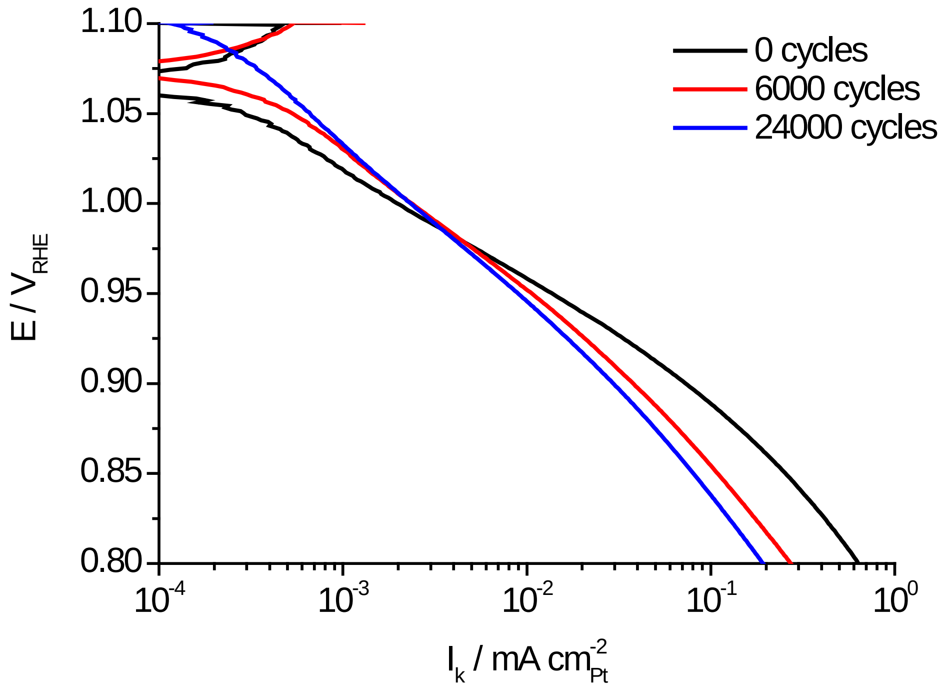


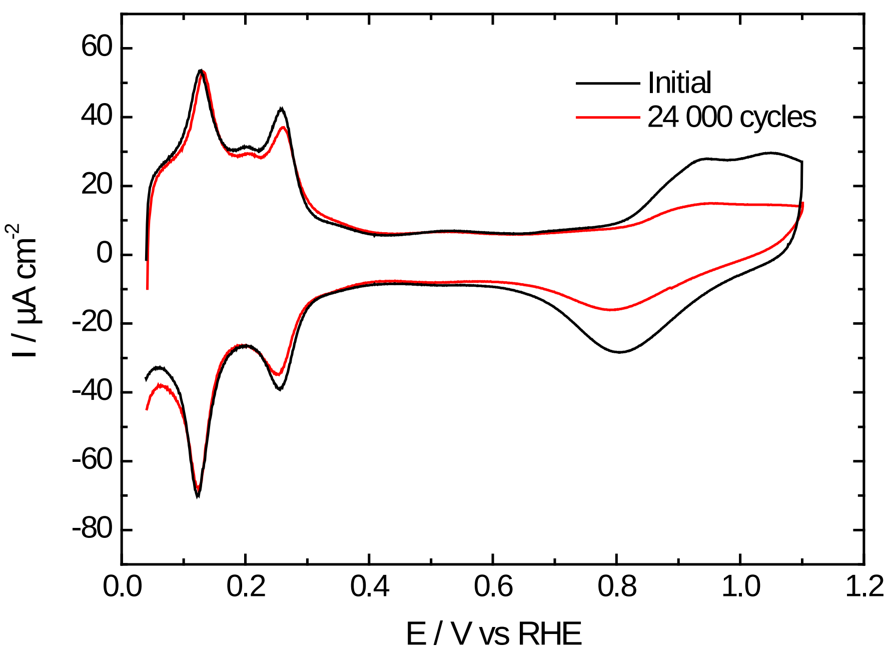




Shut Down – normalised results against ECSA

- ORR specific activity (mA cm^{-2}) increases at E > 1V with repeated cycling of Pt/ATO catalyst
- Tafel slope changes from ~60 to ~80 mV/dec
- Pt oxidation is significantly retarded after potential cycling.
  - Pt-Sb alloy formation? , Increased interaction between Pt and ATO-support?





Conclusions

- Pt/ATO catalyst successfully synthesized
  - Well dispersed, 3.5nm Pt particles on ATO support
- Catalyst ORR activity and ECSA similar to commercial Pt/C
- Increased stability towards AST protocols compared to Pt/C

- Repeated cycling of Pt/ATO catalyst to elevated voltages (>1.2 V) causes significant increase of oxygen reduction activity at voltages above 1V.
  - Cause of reduction in Pt oxidation still unclear

- In situ fuel cell measurements and studies using model electrodes are planned.
  - Comments and cooperation are welcome!

Thank you for your attention

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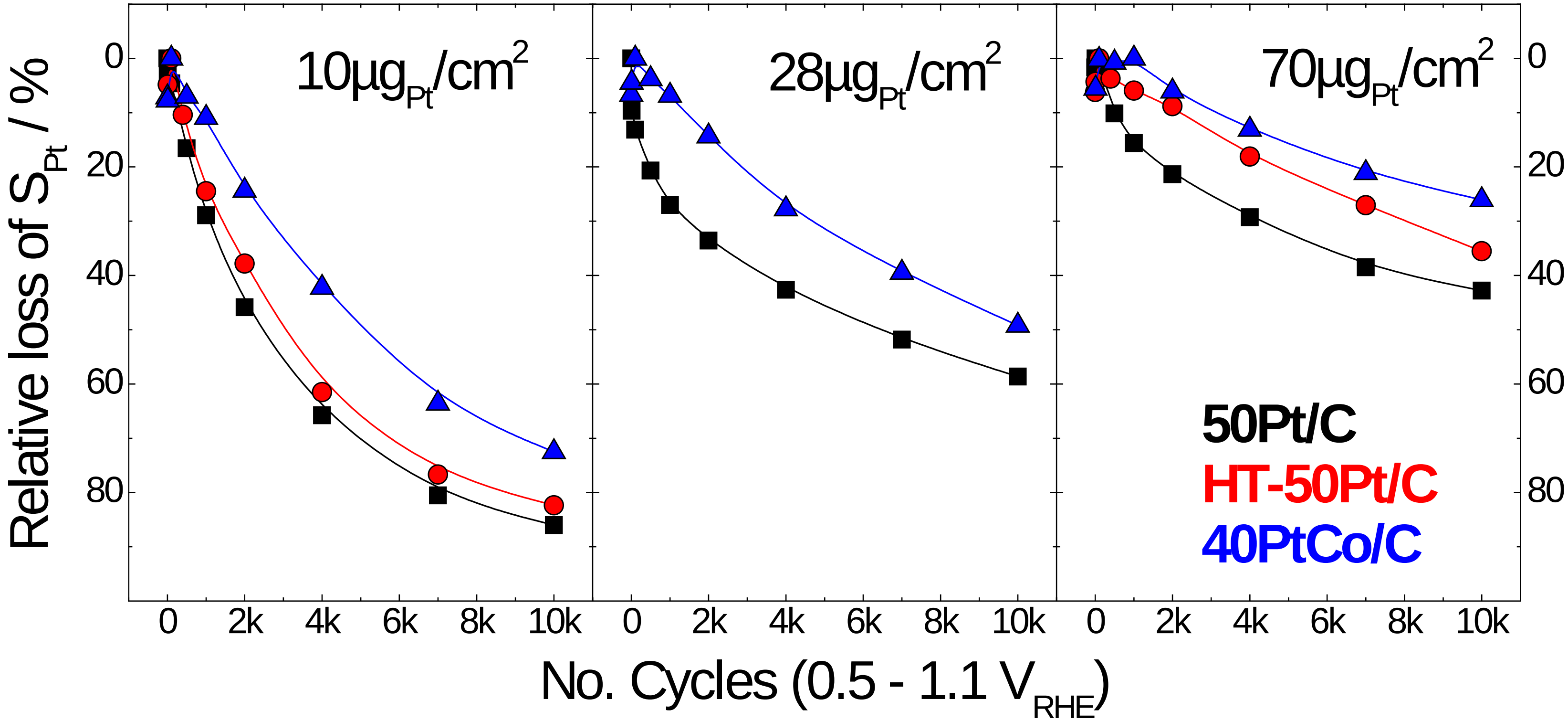
Supporting slides

ADT – Active Pt Surface Area Loss

- Relative ECSA loss as a function of catalyst thin-film (CTF) thickness

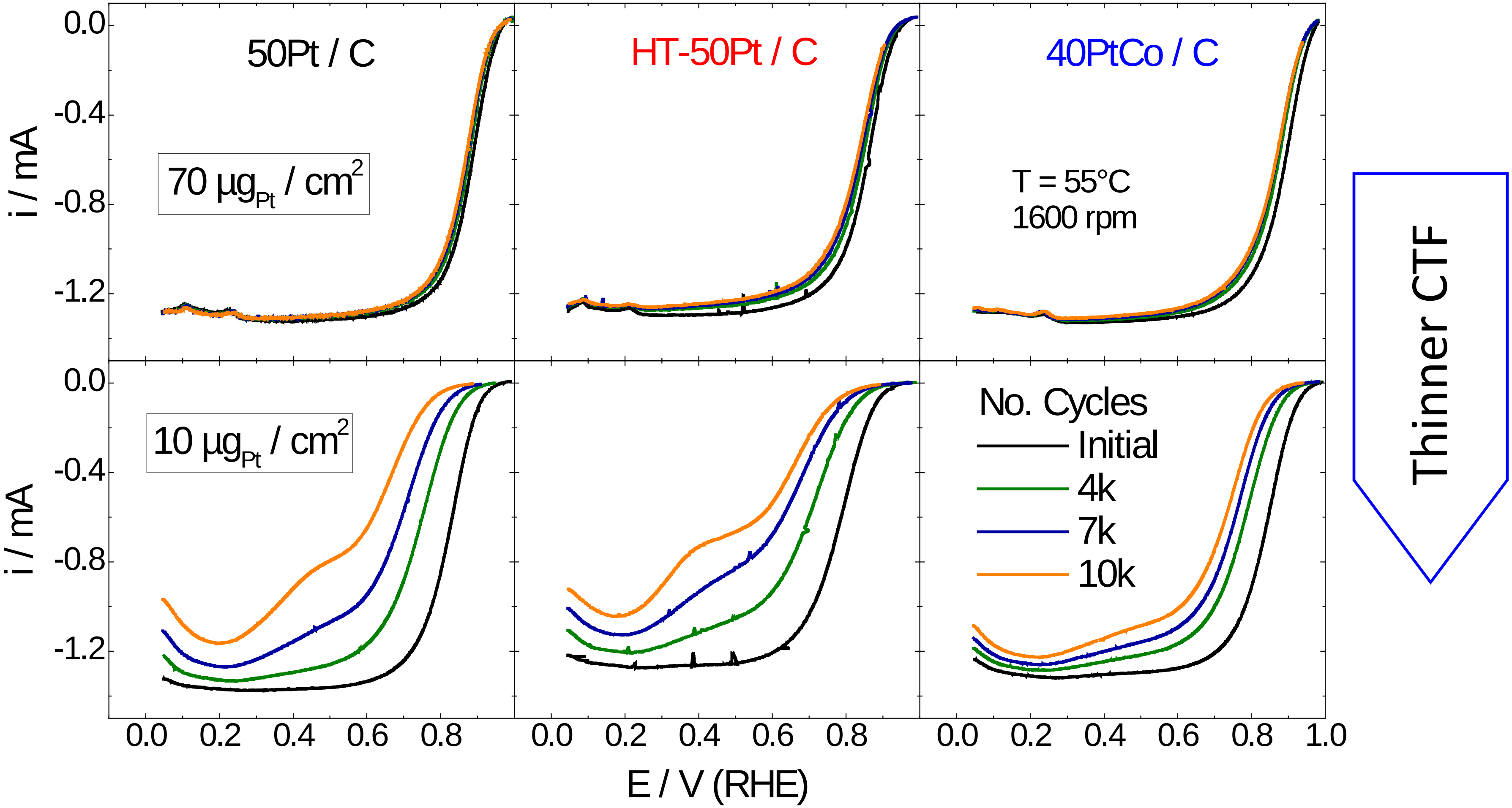


ECSA loss depends on

- CTF thickness, particle size and catalyst composition
- Thinner CTF → smaller probability of Pt redeposition
- Larger particle size → slows down particle growth → smaller ECSA loss
- Pt_3Co/C → smaller relative loss of ECSA in comparison to Pt/C catalysts

ADT – ORR Characteristics

- ORR Activity as a function of catalyst thin-film (CTF) thickness



Thinner CTF → significant decrease in ORR Activity