Hydrogen and Fuel Cells in the Nordic Countries 2013

October 31rd- November 1st 2013

Development of oxide supported electrocatalysts for PEM fuel cells and electrolysers

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SINTEF Materials and Chemistry

Trondheim, Norway

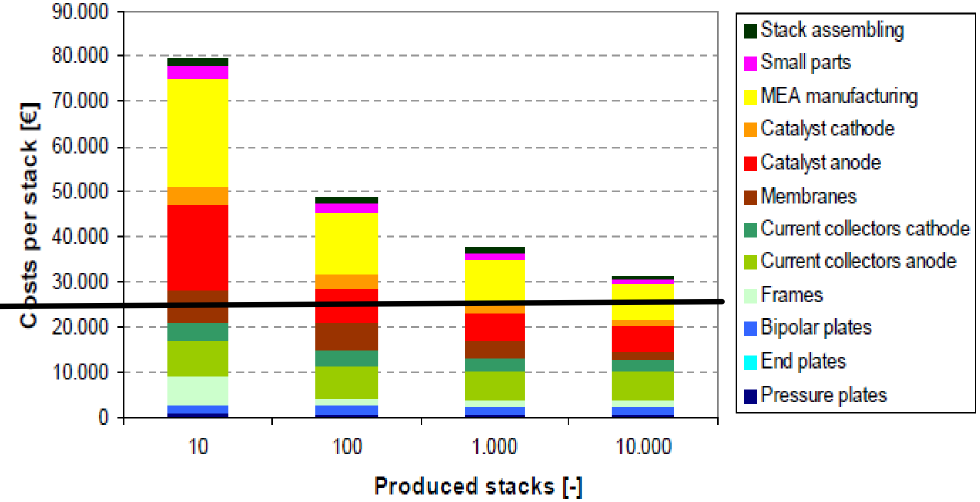
Outline

- Introduction
- Description of target catalyst system
- Ir based catalysts for oxygen evolution
  - Electrochemical characterisation
  - PEM Electrolyser performance
- Pt based catalysts for oxygen reduction
  - Electrochemical characterisation
  - Catalyst stability
- Conclusions

Introduction

Cost and Durability

NEXPEL Projected stack cost



DOE 2015 target
225 €/kW

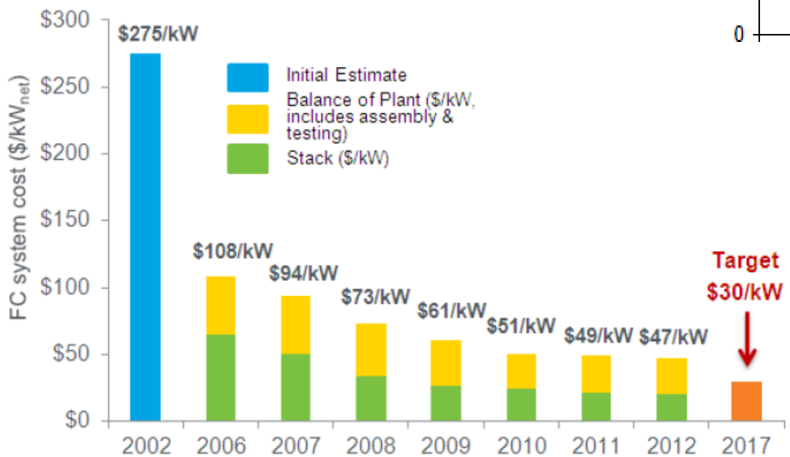
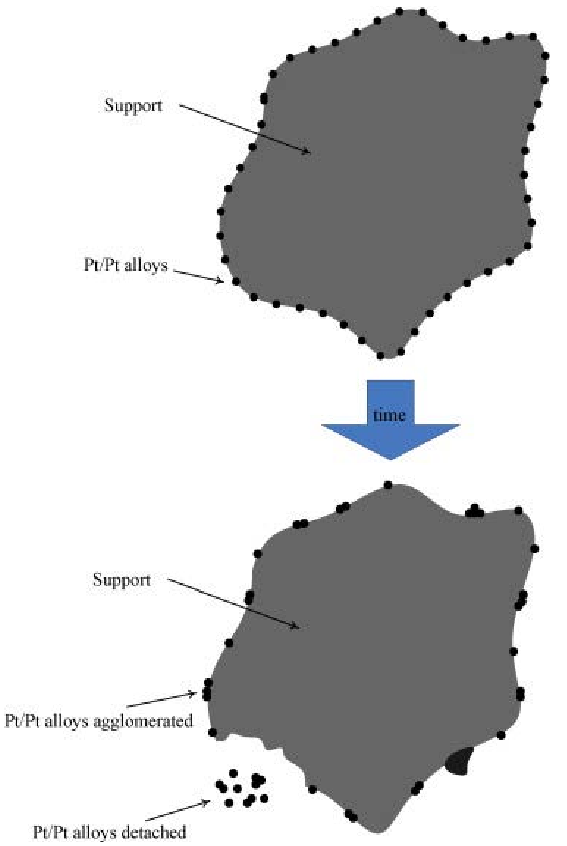


Figure 1. Modeled cost of an 80-kW$_{net}$ PEM fuel cell system based on projection to high-volume manufacturing (500,000 units/year).

DOE Fuel Cell Technologies Program Record #12020

Introduction

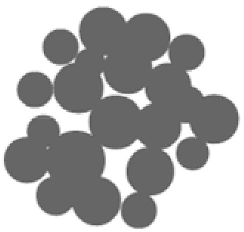
- Catalyst degradation is one of the main causes of reduction of PEM fuel cell performance
- Loss of catalyst active surface area
  - Sintering, dissolution/precipitation
- Corrosion of catalyst support
  - Loss of catalyst/support contact
  - Changes in surface chemistry
  - Collapse of catalyst layer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



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

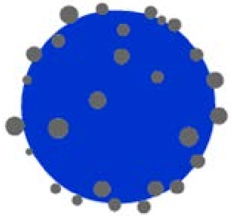
Introduction

- Increase catalytic activity and stability of O_2 evolution catalysts by utilization of a support
  - Increase active surface area
  - Increase catalyst utilization
  - Reduce catalyst particle sintering by support stabilization
  - Increase specific catalytic activity by catalyst support interaction?

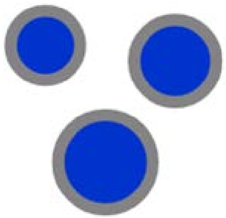


<u>Challenges</u>

- High surface area support
- Stable at elevated voltages and acidic environment for several 1000s hours.



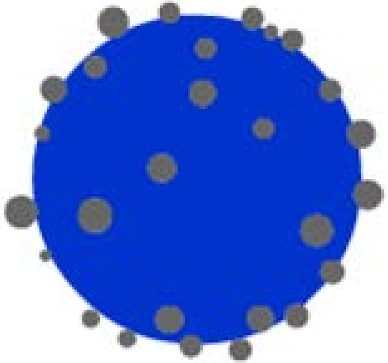
Supported catalyst

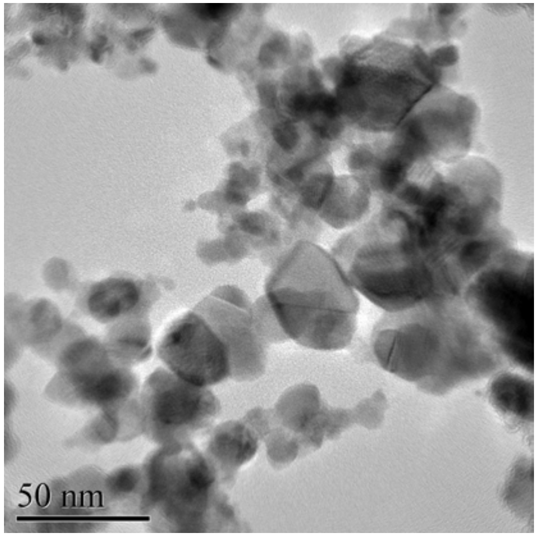


Core-shell structure

Targeted catalyst composition and morphology

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

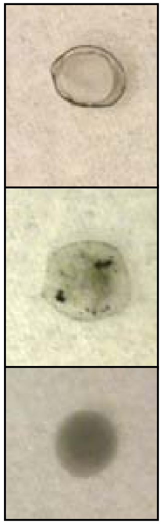




BET surface area : 37 m^2g^{-1}
Particle size: 10-50 nm
Doping level: 7-11 % Sb
High stability in acidic media and at elevated potentials
Relatively high electronic conductivity (> 10^{-3} S cm^{-1})

Thin-film Working Electrode Preparation

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

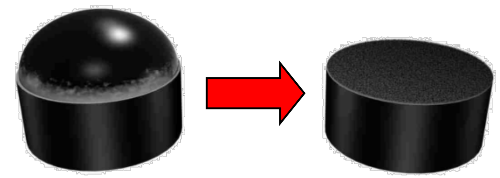


Only Milli-Q water (pH 7)

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

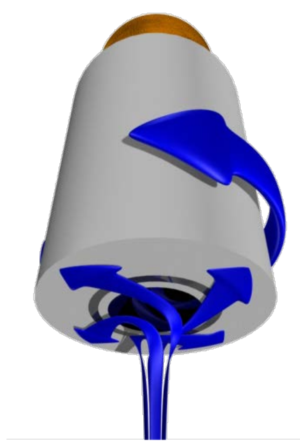
Milli-Q water at pH 3

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

Catalyst deposited = 20 ± 3(7%) μg

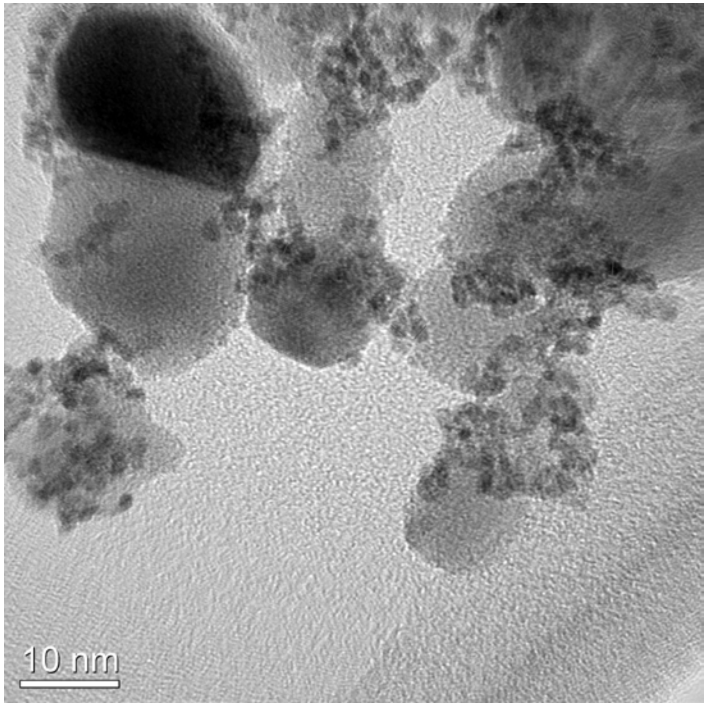


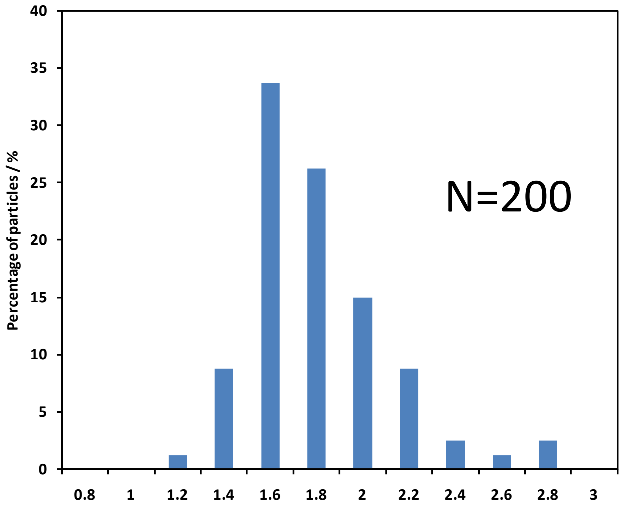
3. Rotating Disk Electrode

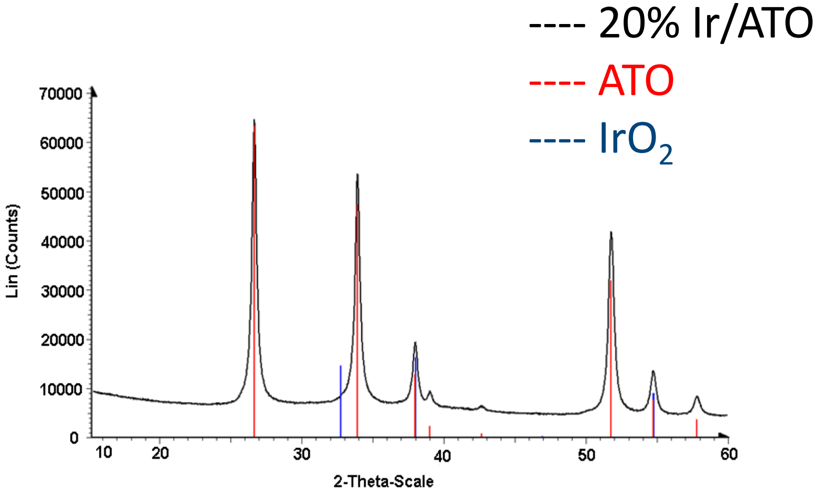
(Pine Instrument) is used for performing the electrochemical measurements in 0.5 M H_2SO_4 electrolyte geometric area: 0.196 cm^2

Oxygen evolution catalysts: Ir/ATO

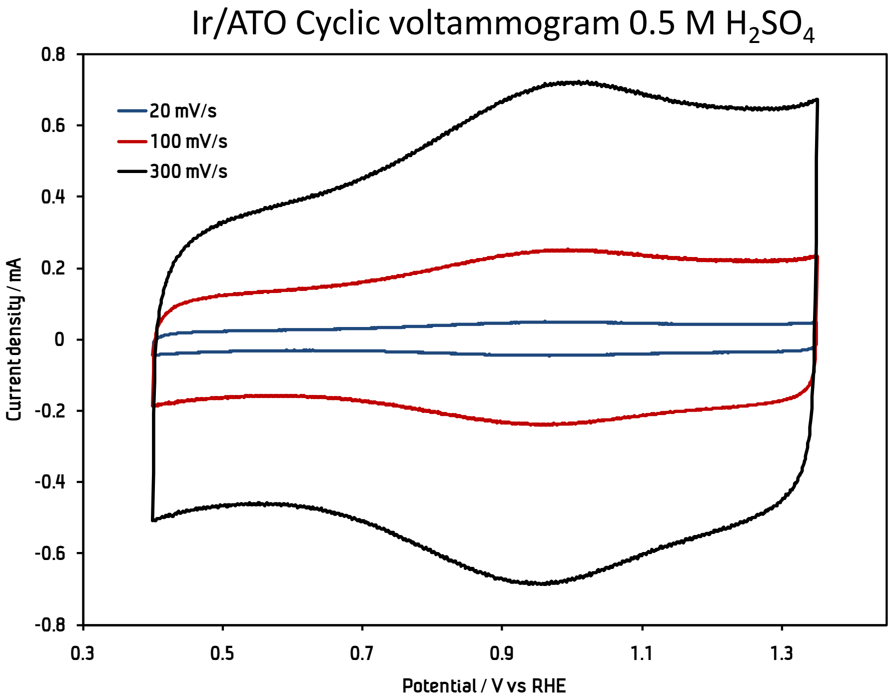
- Average particle size 1.8 ± 0.3 nm
- Crystalline Ir nanoparticles

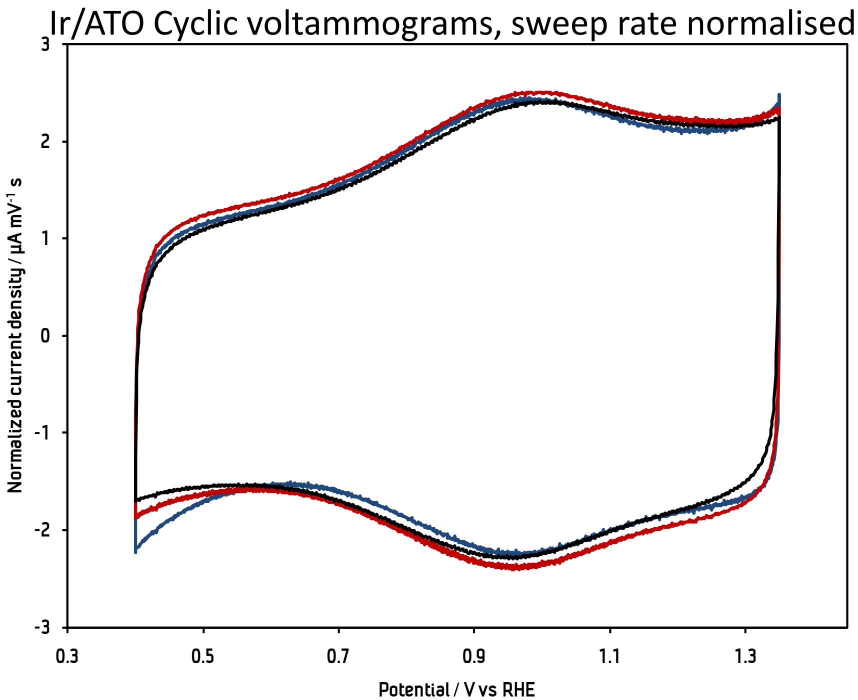






Cyclic Voltammetry





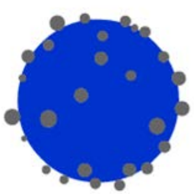
$$\mathrm{IrO_a(OH)_b \rightleftharpoons IrO_{a+\delta}(OH)_{b-\delta} + \delta H^+ + \delta e^-}$$

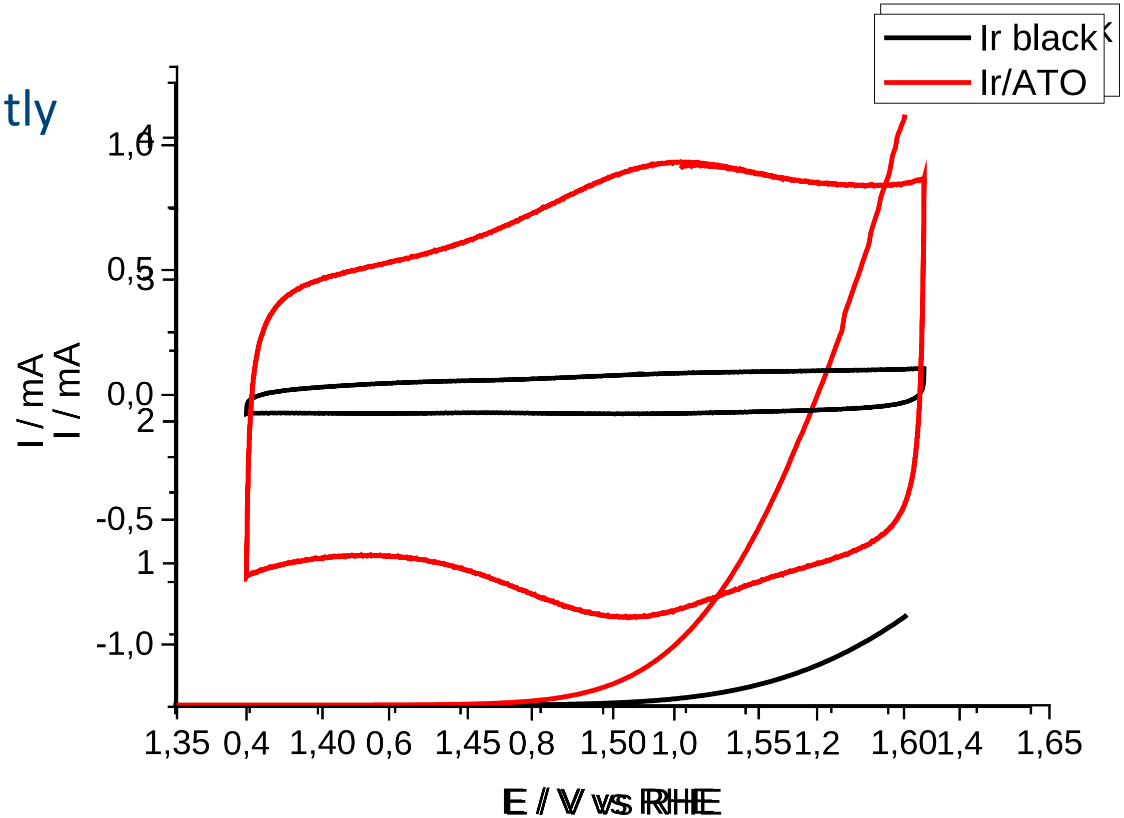
80-90% of Ir is intercalating H^+ ➡ Complete oxidation of Ir to IrO_2

D. Michell, D. Rand, R Woods. J Electroanal. Chem., 1978, 89, 11-27

Effect of support

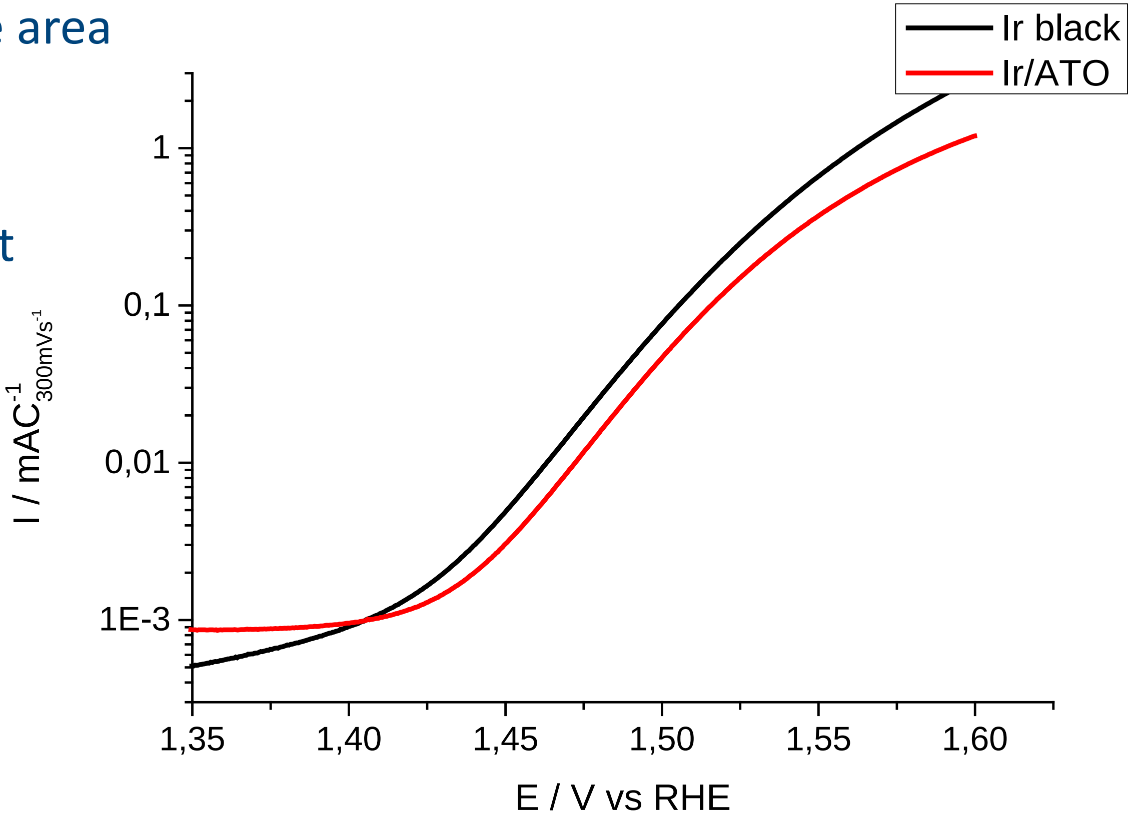
- 10x increase of "surface area"
- Catalyst activity significantly higher





Origin of catalyst activity increase

- Similar activity after normalising against surface area
- Increased catalytic activity due to higher surface area
- No signs of catalyst-support interaction



MEA performance

Nafion 117, 80 °C

Cathode:

20wt% Pt/C

1 mg /cm^2

Anode:

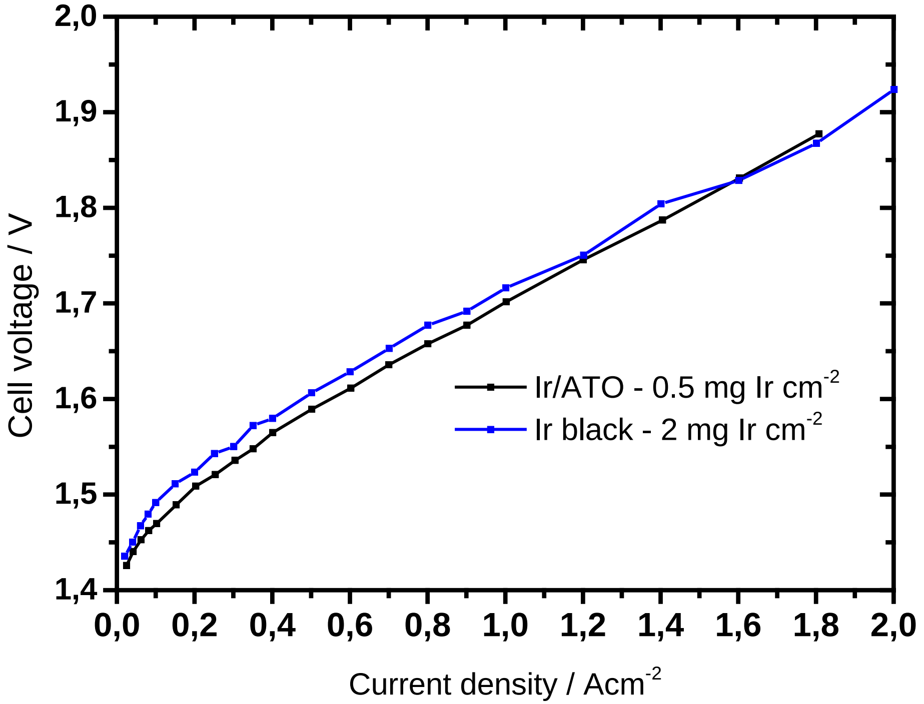
20 wt% Ir/ATO

0.5 mg/cm^2

vs.

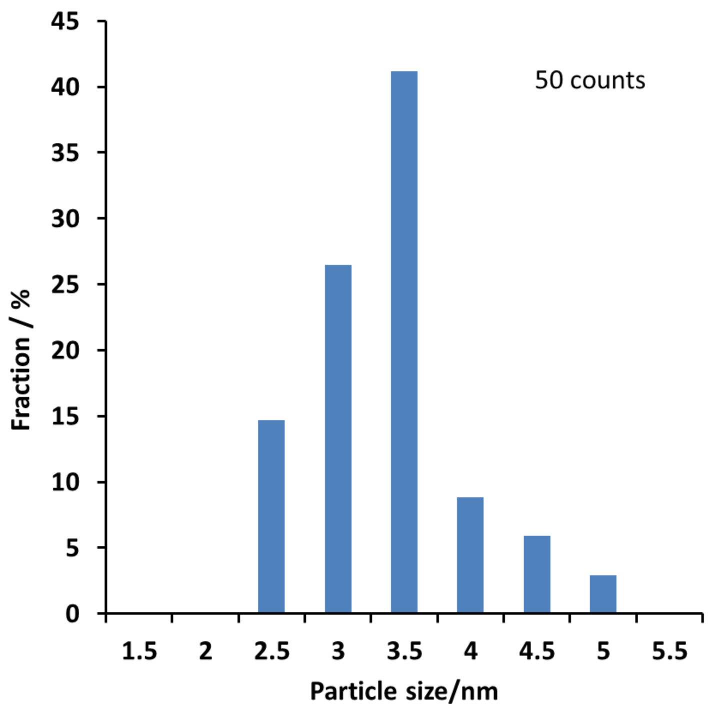
Ir-black

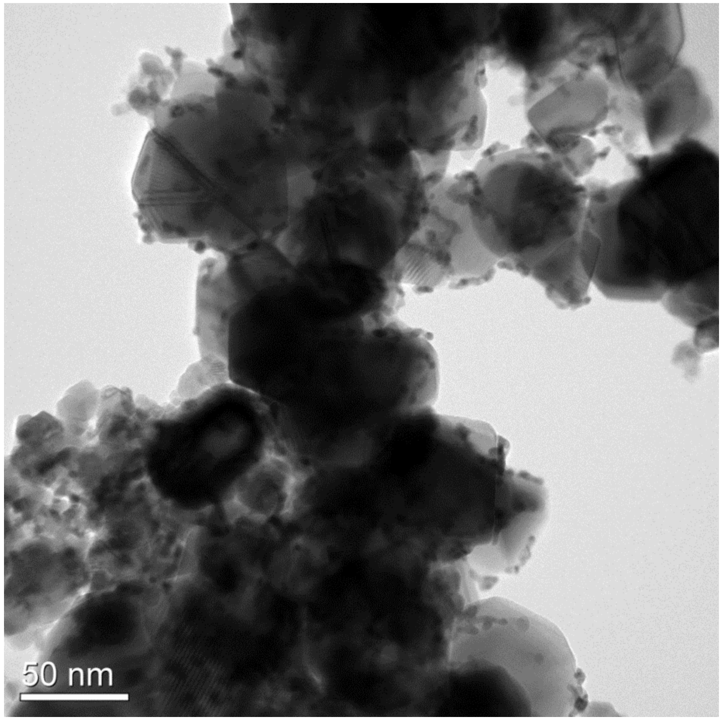
2 mg/cm^2



Oxygen reduction catalysts: Pt/ATO

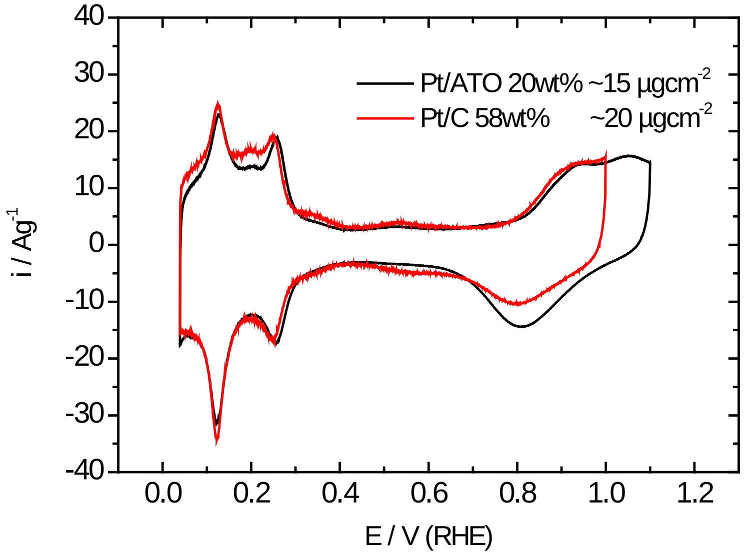
- Average particle size 3.2 nm
- Well dispersed on ATO surface

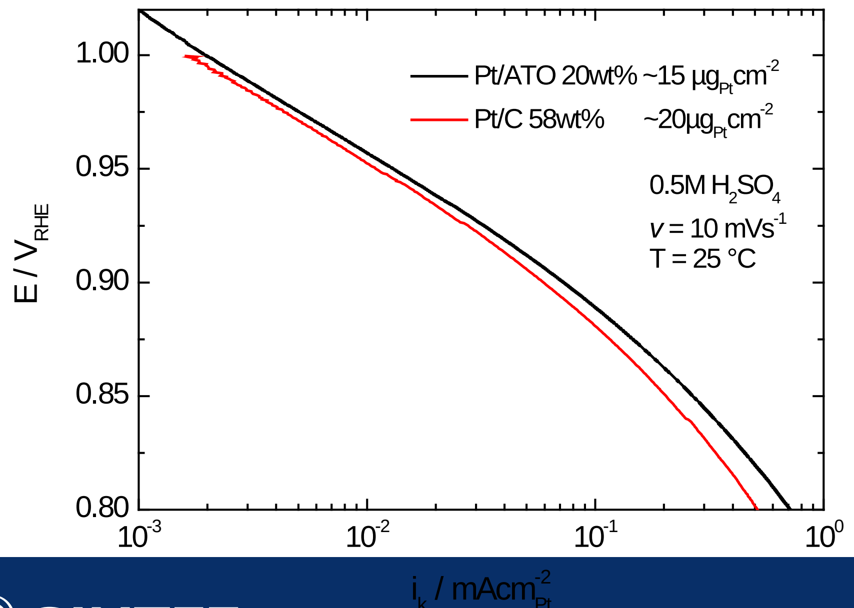


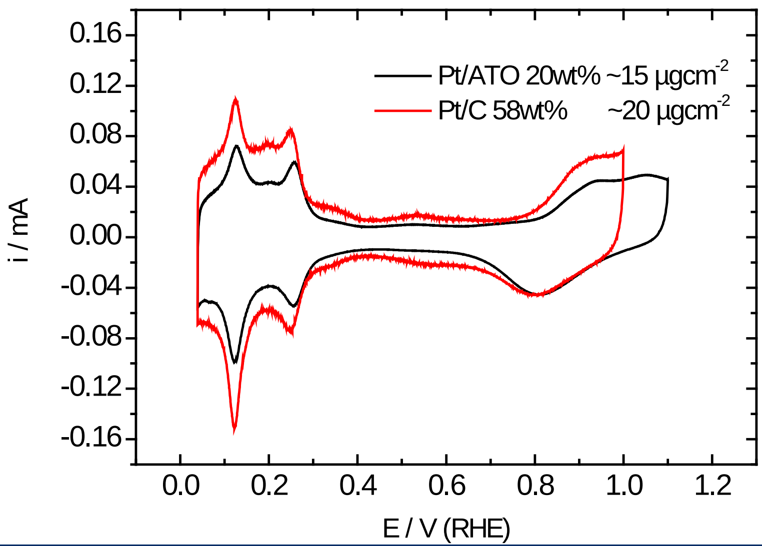


Pt/ATO vs Pt/C

- 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})

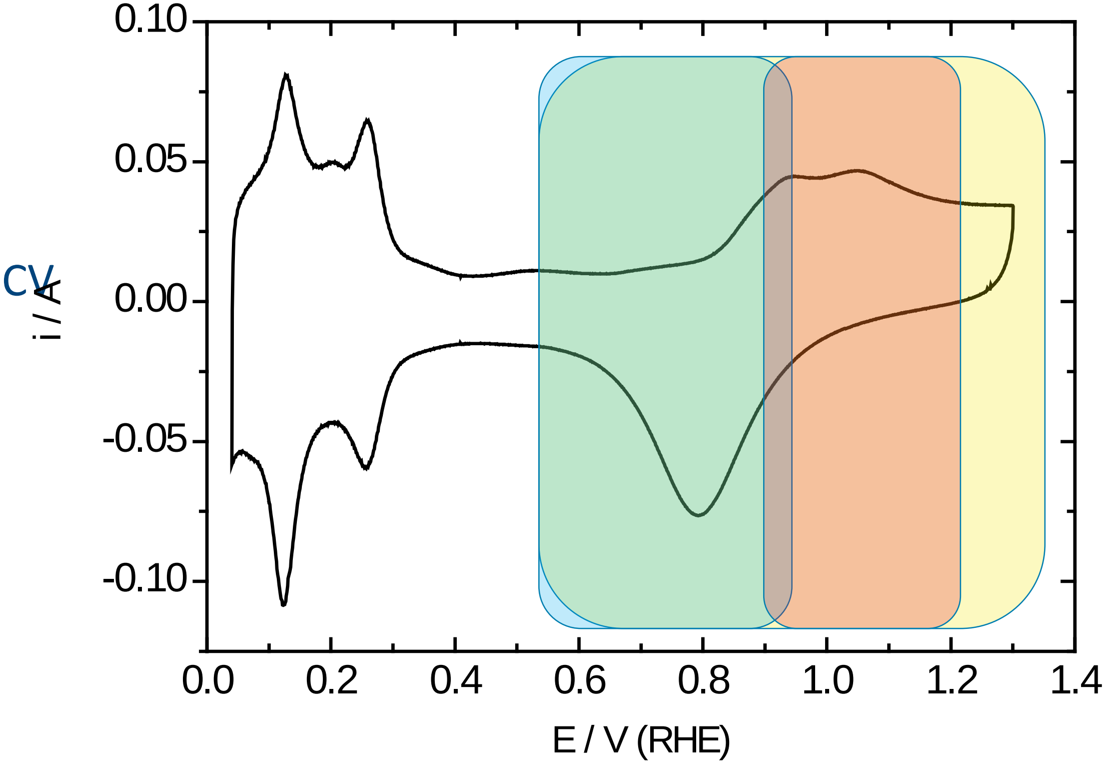






AST Protocols

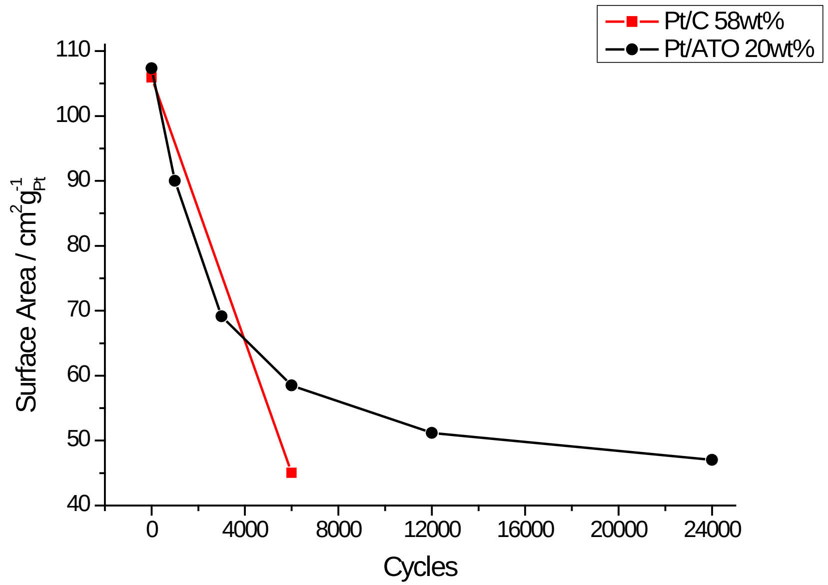
- Catalyst stability evaluated against three different AST protocols
- Load cycling (0.55-0.95V):
  - Mimic normal FC operation.
  - Pt catalyst in reduced state
- Start up (0.9-1.2V):
  - Elevated potentials due to OCV and gas purge
  - Catalyst in oxidized state
- Shut down (0.55-1.35V)
  - Elevated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

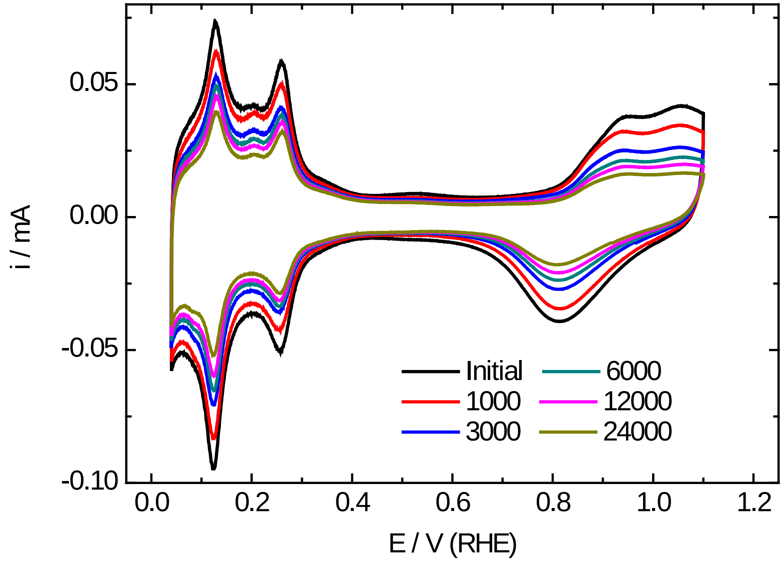


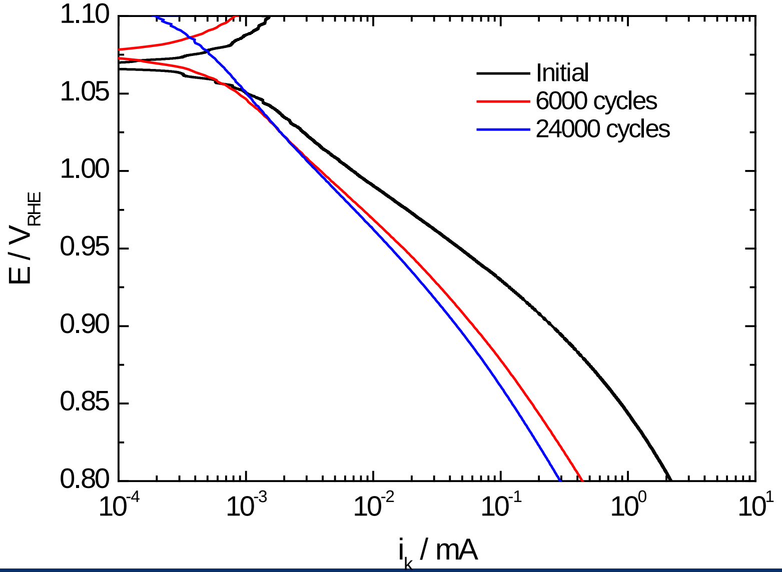
Results - Shut Down

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

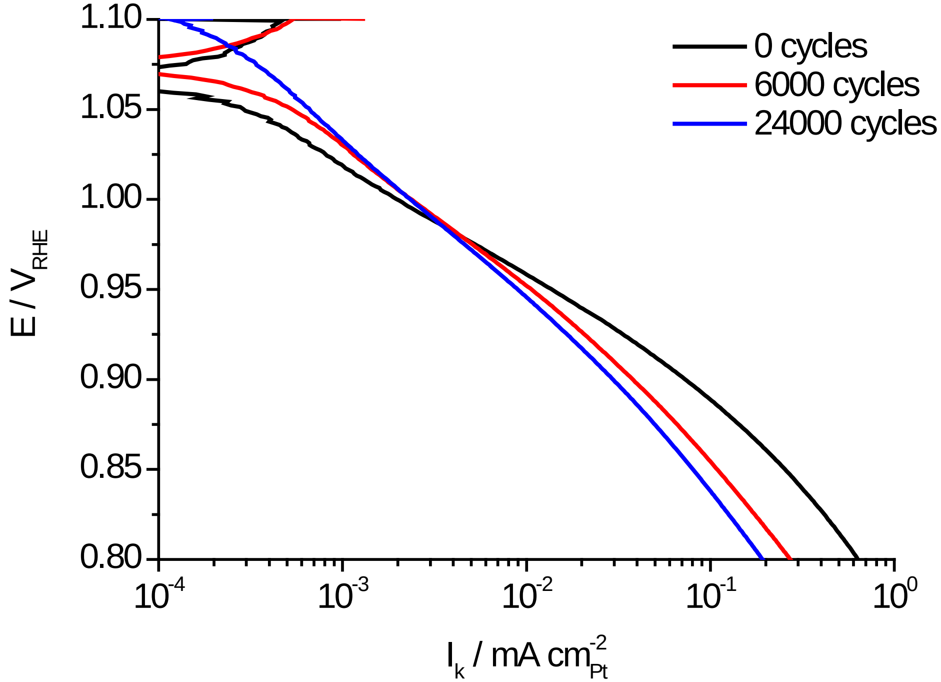


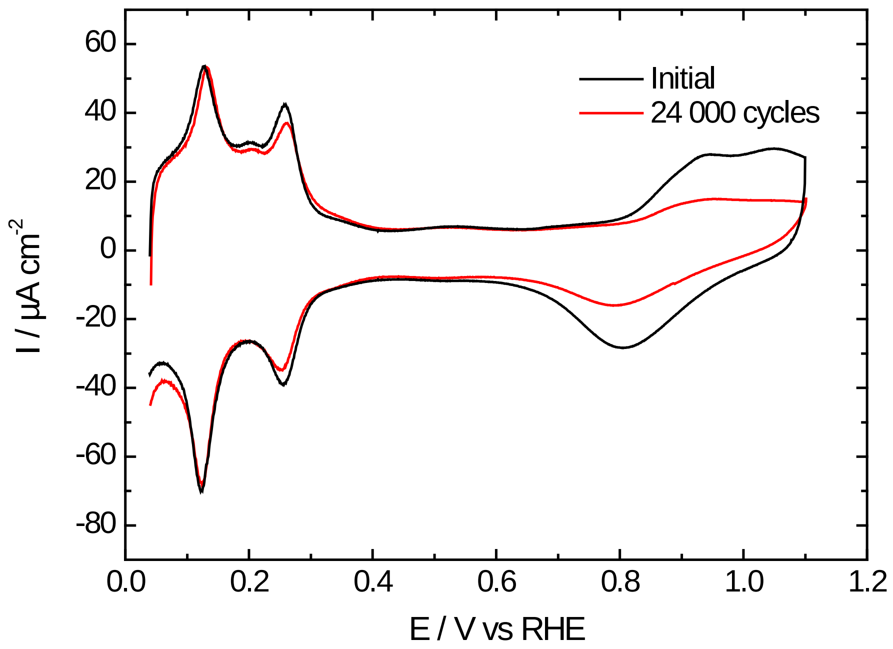




Shut Down – normalised results against ECSA

- 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?





The next step; NOVEL

NOVEL

- Continuation of novel materials development
  - New catalysts and catalyst supports
  - Radiation grafted membranes
  - Coatings of bipolar plates and current collectors
- System design and optimization
- Increased understanding of lifetime and degradation issues in PEM electrolysers

SINTEF

JM Johnson Matthey Fuel Cells *the power within*

Fraunhofer ISE

PAUL SCHERRER INSTITUT PSI

cea

Beneq

TEER COATINGS LTD innovation and experience

HELION HYDROGEN POWER

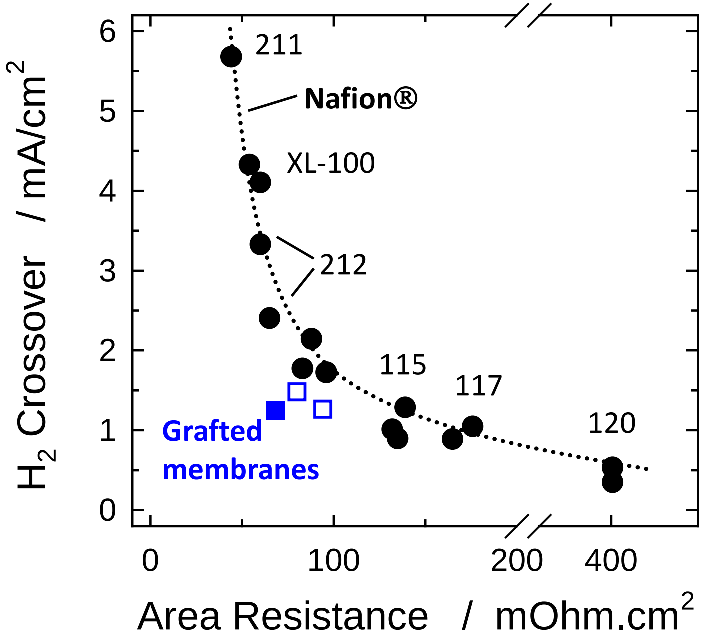
NOVEL, Preliminary results

- New oxygen evolution catalyst developed with 75% higher electronic conductivity
  - 20wt% $Ir/Nb_xTi_{(1-x)}O_2$
  - Similar activity to Ir/ATO
- Irradiation grafted membranes with higher "figure of merit"
  - ETFE Base polymer with Acrylonitrile as Co-monomer

Figure of merit:

Nafion®: 5.8 ± 1.3
Grafted membranes: 9.5 ± 1.9

30cm² cell, 80°C, H_2/O_2 stoich. 1.5/1.5, full humidification, 2.5 bar_a



SMARTCat

FCH JU collaborative project starting on June 2013

Systematic, **M**aterial-oriented **A**pproach using **R**ational design to develop break-**T**hrough **Cat**alysts for automotive PEMFC

Main goal:

Develop a new electrode concept based on ternary alloyed/core shell catalyst clusters supported on conductive metal-oxide for automotive PEMFC applications

N°	Participant	Country	Type
1 (Coord.)	CNRS – *Gremi*	France	R&D
2	SINTEF	Norway	R&D
3	Tech. Uni. Denmark	Denmark	R&D
4	CEA	France	R&D
5	Basic Membranes	Netherlands	Industry

SINTEF main activity (WP Leader)

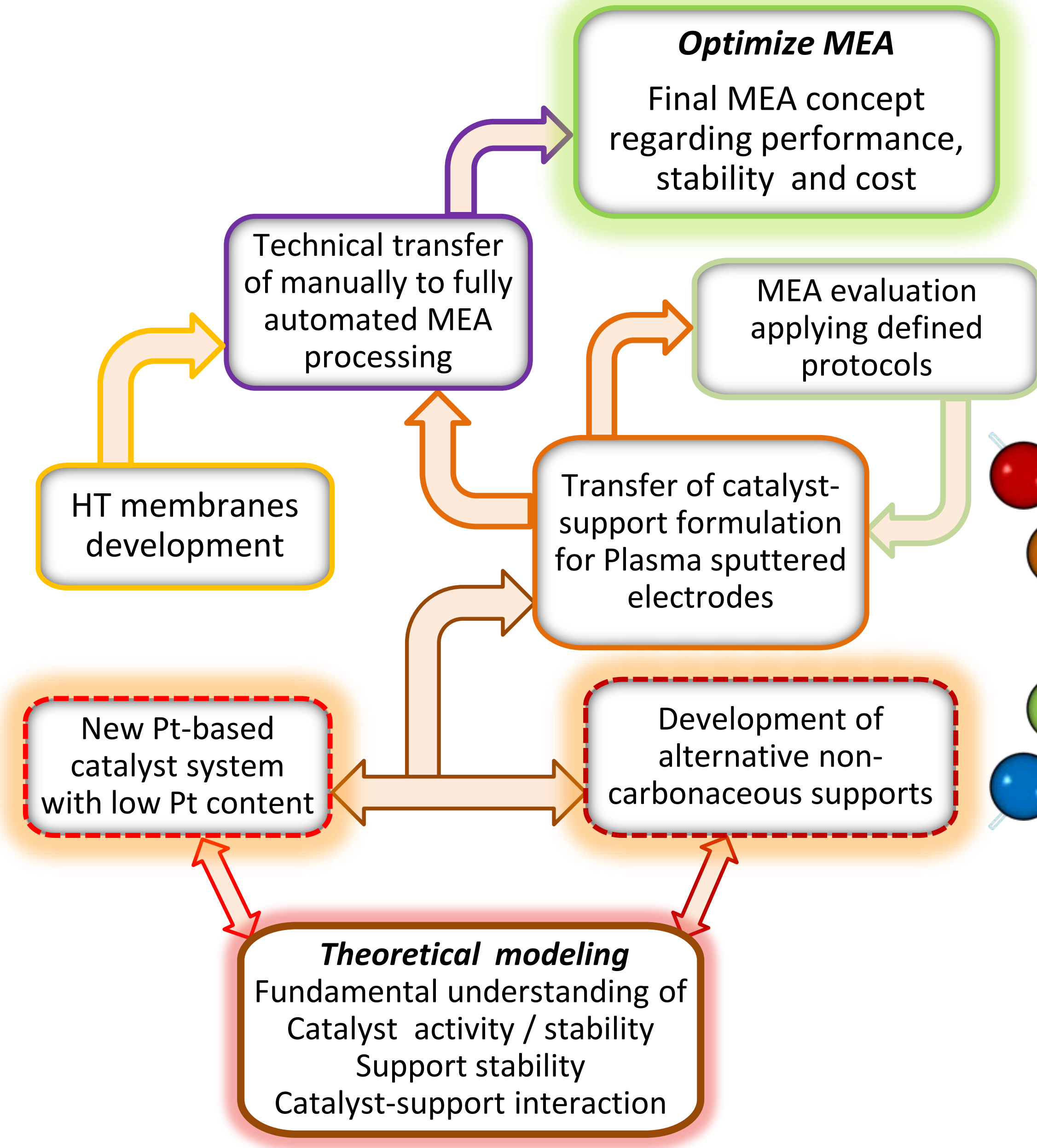
Develop a robust conductive oxide-based material as cathode catalyst support

June 2013 - May 2017

Total Budget: € 4,963,497

SINTEF's budget: € 1,028,184

SMARTCat



- *WP1 Specifications*
- *WP2 Tri-metallic Catalysts & Electrodes*
- *WP3 Highly corrosion resistant catalyst support*
- *WP4 Optimization of MEA processing*
- *WP5 FC testing and demonstration.*

*These project has received funding from the European Community's Seventh Framework Programme (**FP7/2007-2013**) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° [**325327**]*

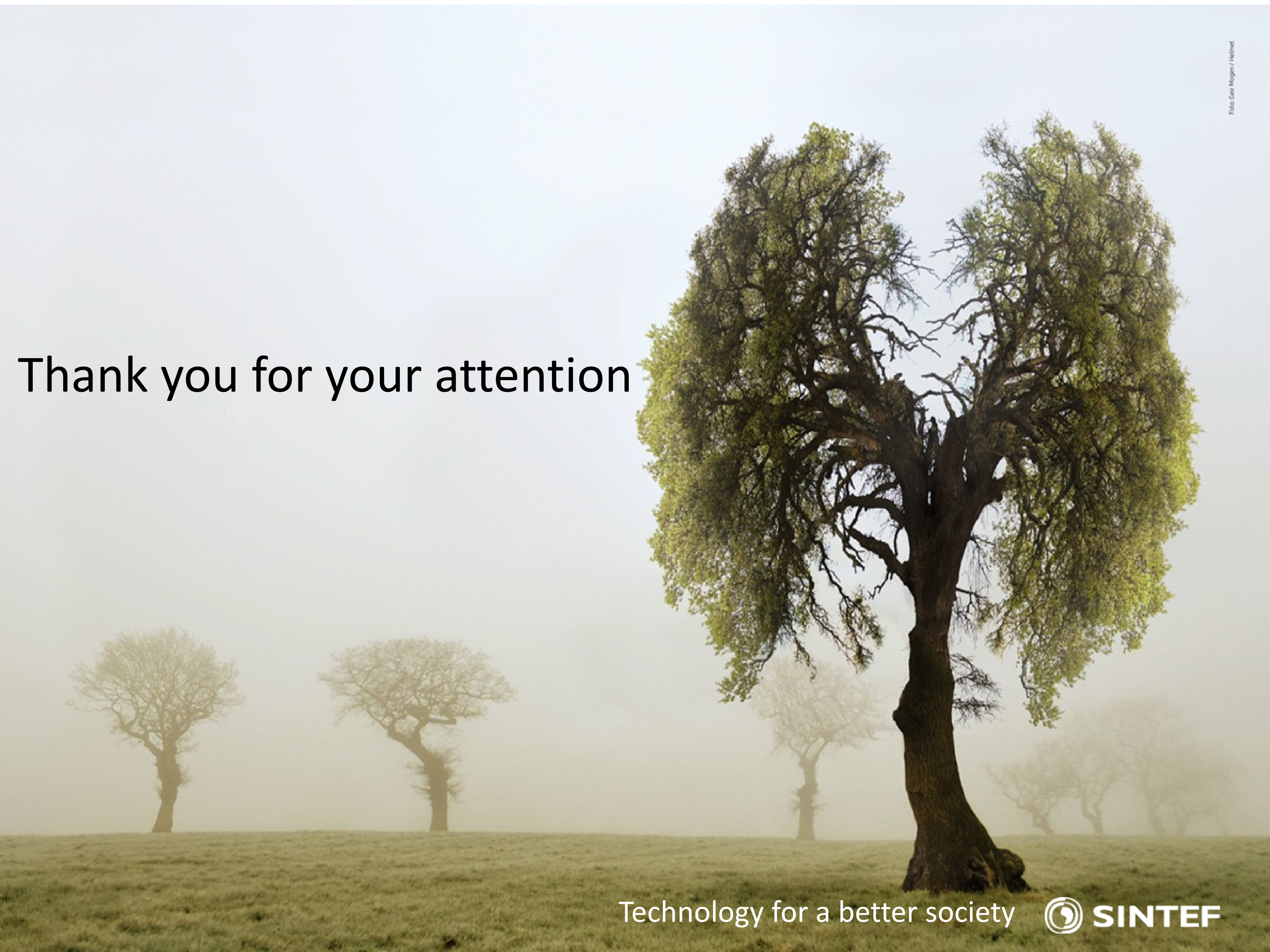
Conclusions

- Antimony Tin Oxide (ATO) has been demonstrated as a possible support material for both oxygen evolution and reduction catalysts in PEM cells.

- Initial tests show that Ir and Pt nanoparticles supported on ATO have good durability using AST protocols.

- Further investigations needed to investigate long term stability
  - Dopant removal – loss of conductivity

- Development of other oxide supports and bi/trimetallic catalyst alloys is ongoing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Technology for a better society
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