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SUPPORTED CATALYST PARTICLES FOR PEM FUEL CELLS BY ONE-STEP FLAME SYNTHESIS

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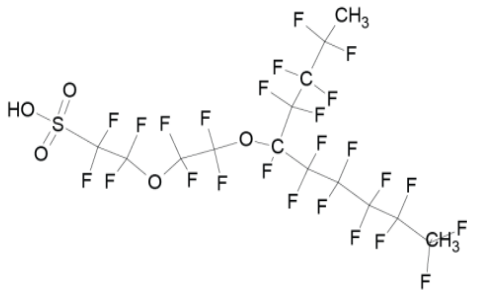
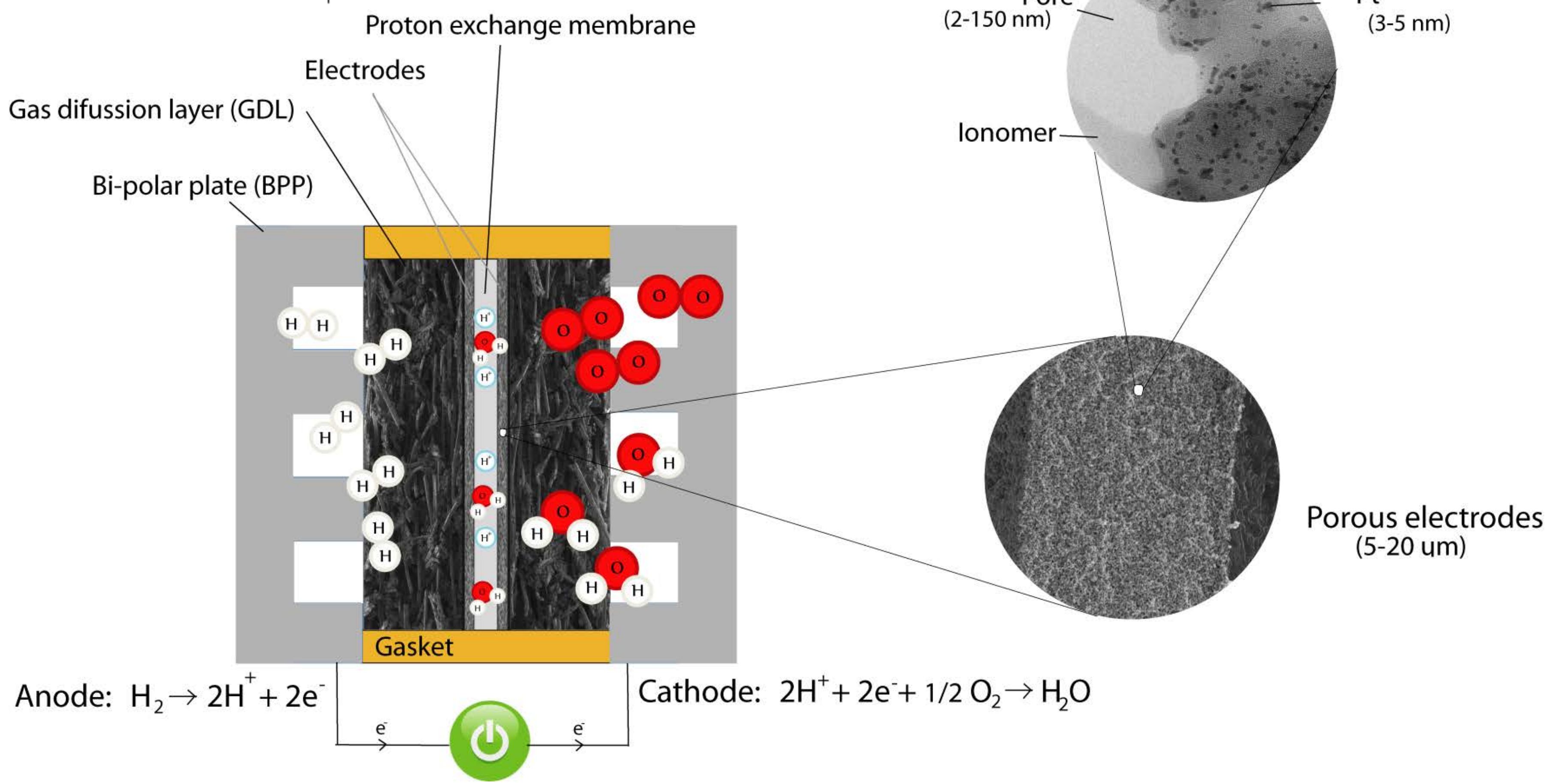
Electrodes for PEM fuel cells



Nafion® ionomer



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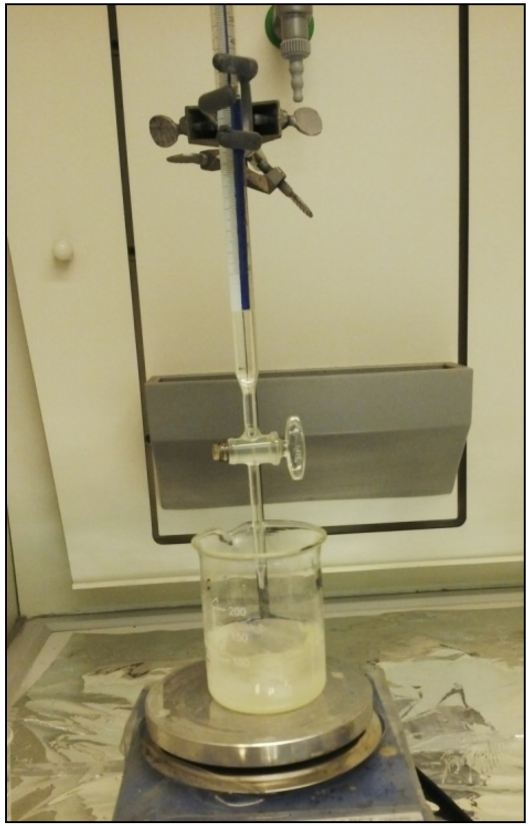
Cathode catalyst support materials

- State-of-the-art: Carbon blacks
- Alternative materials: Metal oxides
- Proposed use of SnO_2 based materials with defined criteria:
  1) Conductivity (σ): Min 0.01-0.1 Scm^{-1} (>1 Scm^{-1} for support + catalyst)
  2) BET Surface Area (SA_{BET}): >50 m^2g^{-1}
  3) Microstructure – Pore Size Distribution (PSD): 20 – 150 nm
- Conductivity tailored by doping (Sb and Nb) and post treatment
- Evaluation of two synthesis processes (FSP and Co-P) for obtaining given microstructure and surface area

Synthesis of catalyst supports: $Sn_{1-x-y}Sb_xNb_yO_2$ $(x + y \leq 0.15)$

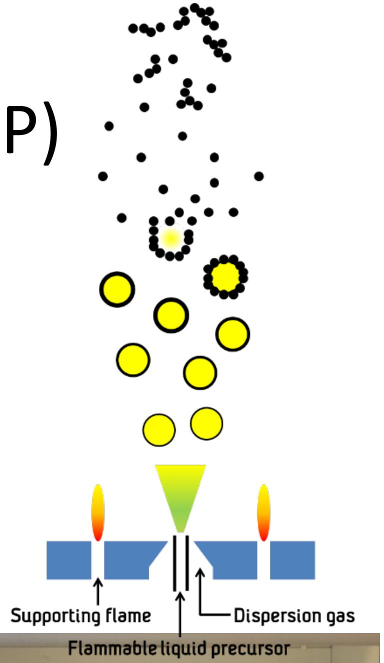
❑ Co-precipitation (Co-P)

- Solvent: isopropanol
- Precursors
  - Tin (II) chloride
  - Antimony (III) chloride
  - Niobium (V) ethoxide
- Dropwise addition into 2M NH_4OH
- Overnight stirring
- Repeated washing/ centrifugation
- Drying, grinding, calcination 550°C for 2 hrs in ambient air



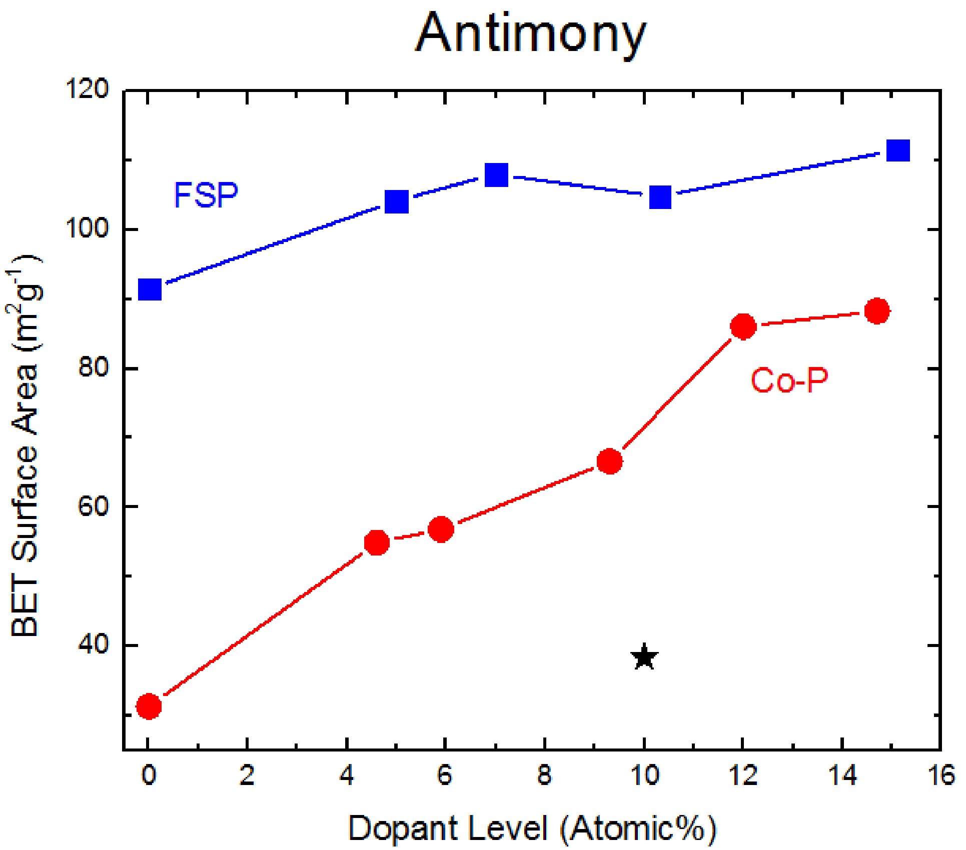
❑ Flame spray pyrolysis (FSP)

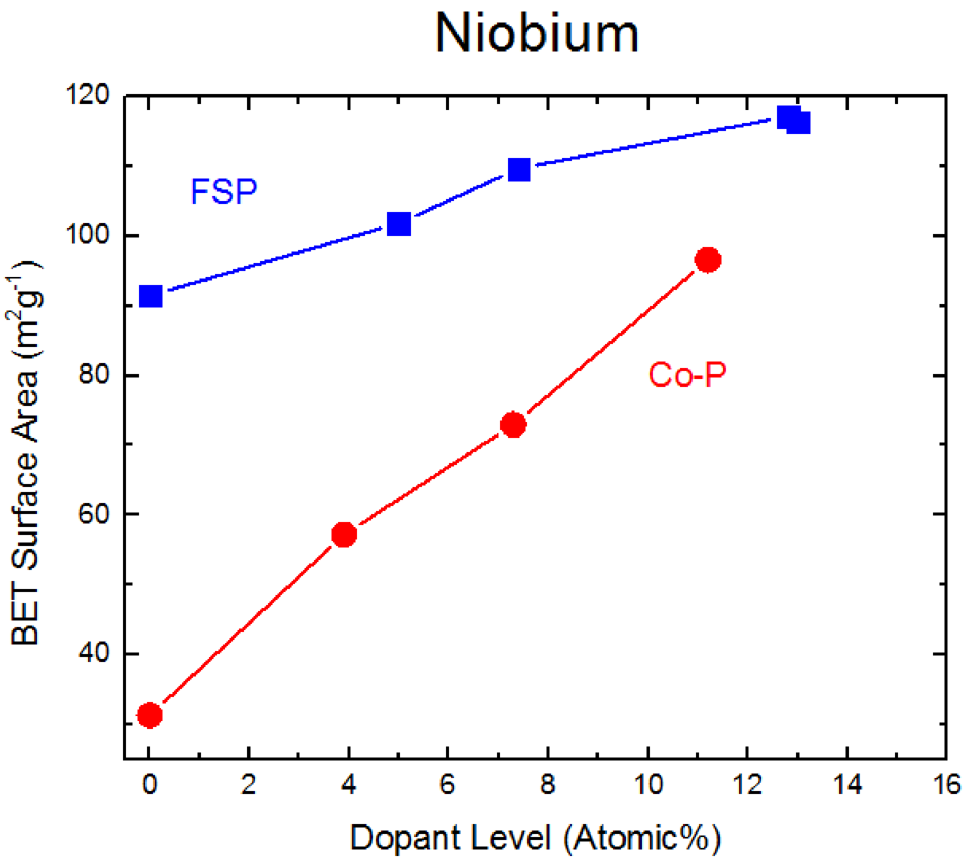
- Solvent: xylene
- Precursors
  - Tin (II) 2-ethylhexanoate
  - Antimony (III) ethoxide
  - Niobium (V) ethoxide
- Operating conditions (Tethis NPS10)
  - Flame: 1.5 L/min CH_4 / 3.2 L/min O_2
  - Dispersion gas (O_2): 5 L/min
  - Liquid flow rate Flame: 5 mL/min



Cathode catalyst support materials

- Effect of synthesis route and doping in SnO_2 on surface area
- Flame spray pyrolysis selected over co-precipitation (also for pore size)





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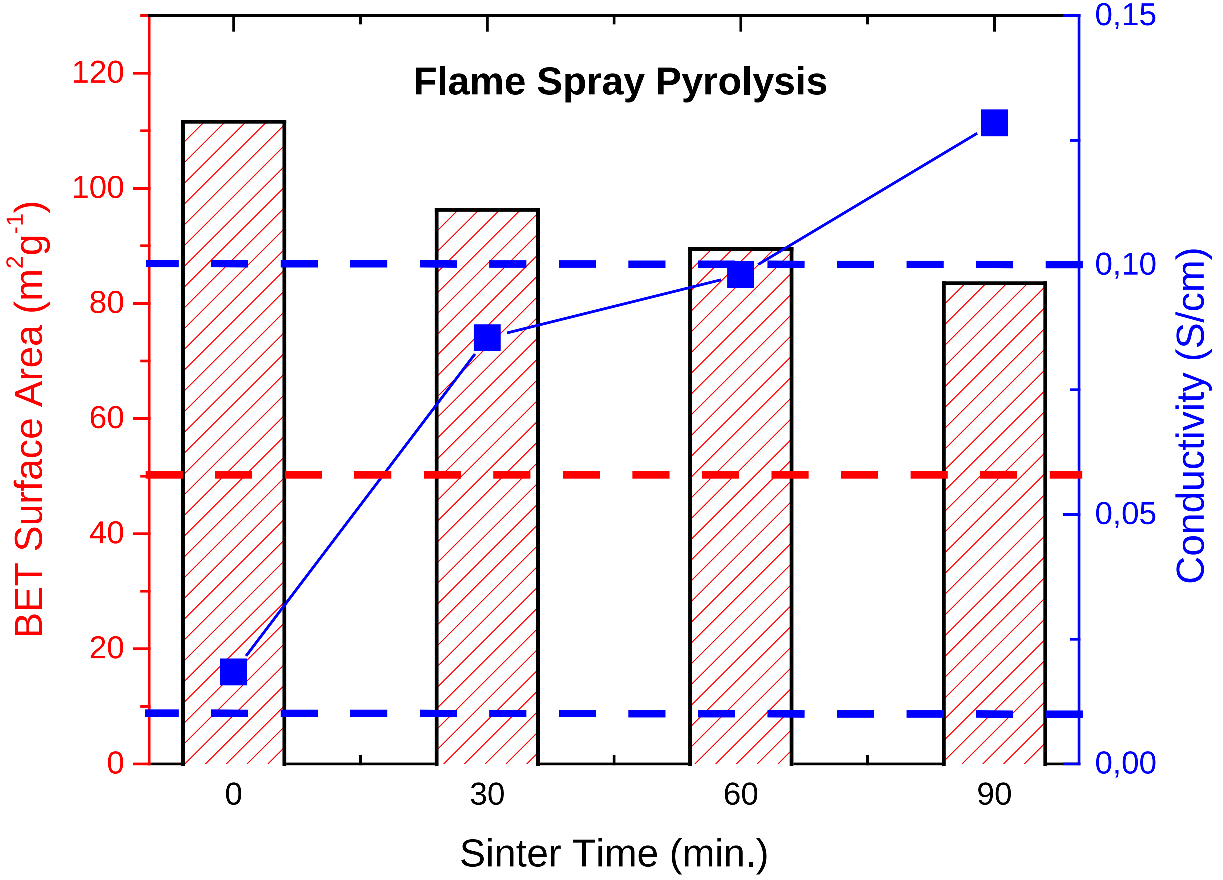
Cathode catalyst support materials

❑ Effect of post treatment, example $Sn_{0.85}Sb_{0.15}O_2$

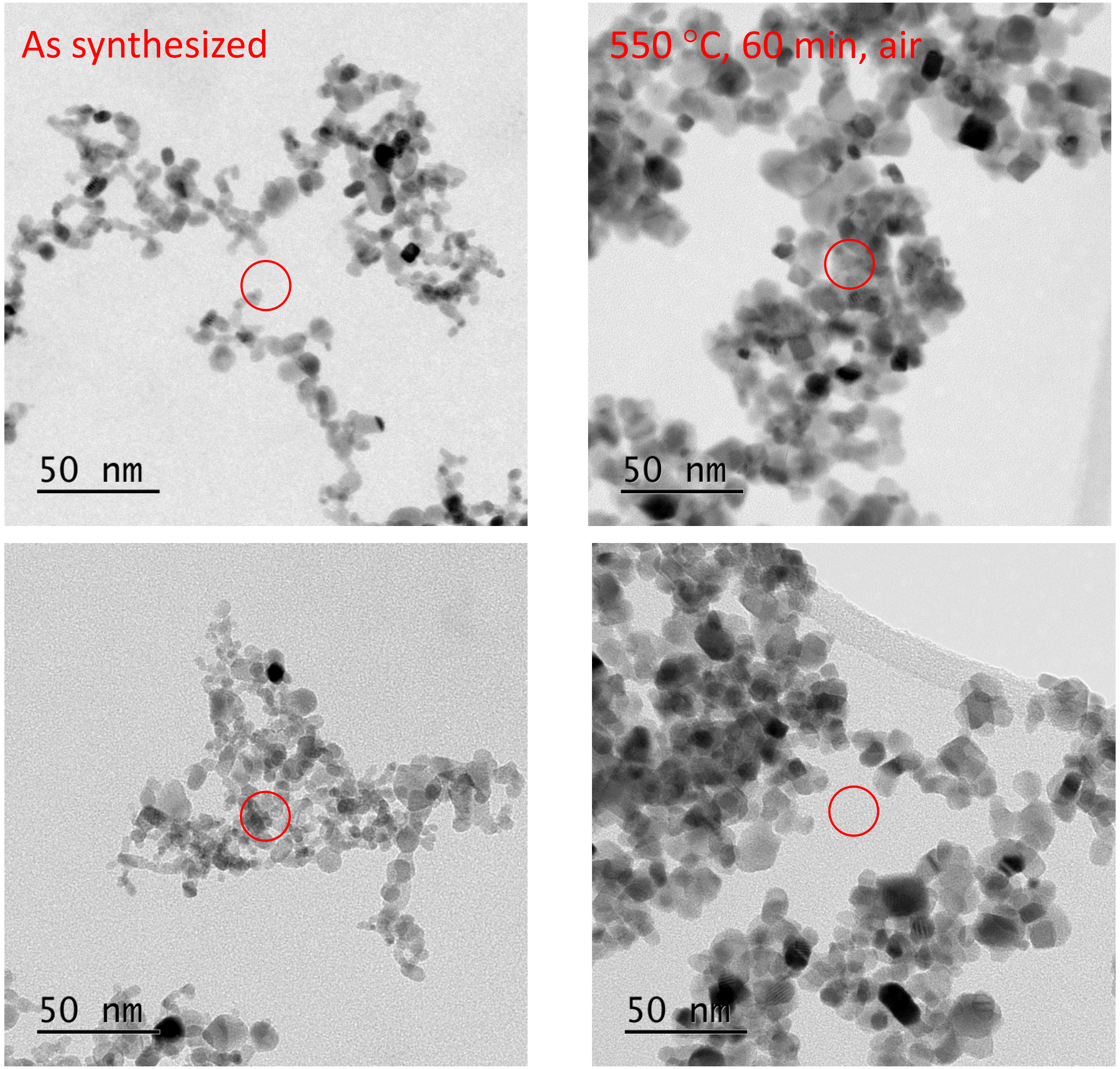
- ➢ Ball milling (YSZ) in iso-propanol (18 hours)
- ➢ Heat treatment at 550°C in ambient air
- ➢ Increased connectivity → increased conductivity
- ➢ Acceptable reduction of surface area



Cathode catalyst support materials

- Tailoring of microstructure

  - Example, $Sn_{0.95}Sb_{0.05}O_2$
  - Heat treatment at 550°C in air for 60 minutes
  - Growth of crystallite size → matching lower PSD range

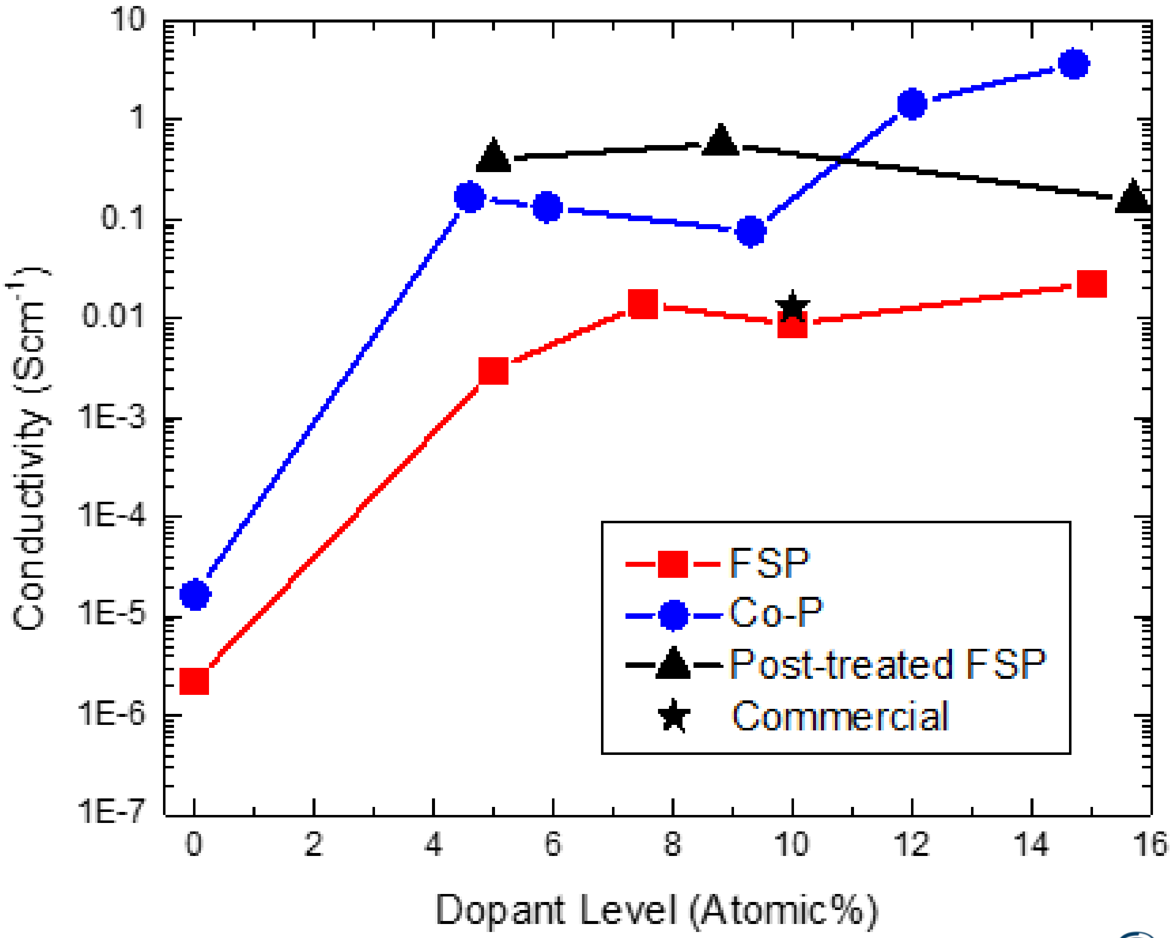


Red circles has a diameter of exactly 20 nm

Cathode catalyst support materials

❑ Effect of Sb-doping and post treatment on conductivity

- ➢ Optimal Sb-doping level of ~7%
- ➢ Co-P powders display higher conductivity than as synthesized FSP powders
- ➢ Post treatment of FSP powders → 2 orders of magnitude higher conductivity



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Pt catalyst deposition

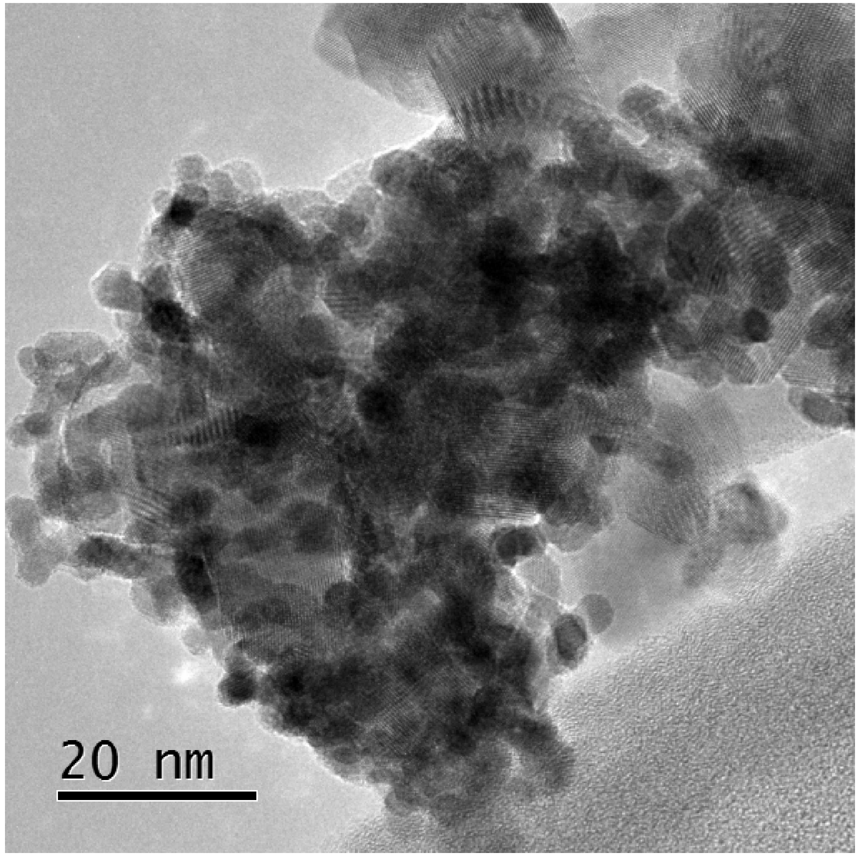
- Three methods evaluated
  - Polyol ("standard")
    - Poly-alcohol acting as reducing agent forming colloidal solution
    - Time consuming and use of chloride precursors
  - Formic acid
    - Fast reaction, less time consuming
    - Still use of chloride precursors
  - FSP
    - Fast, one-step process
    - Non-chloride precursors

Pt catalyst deposition

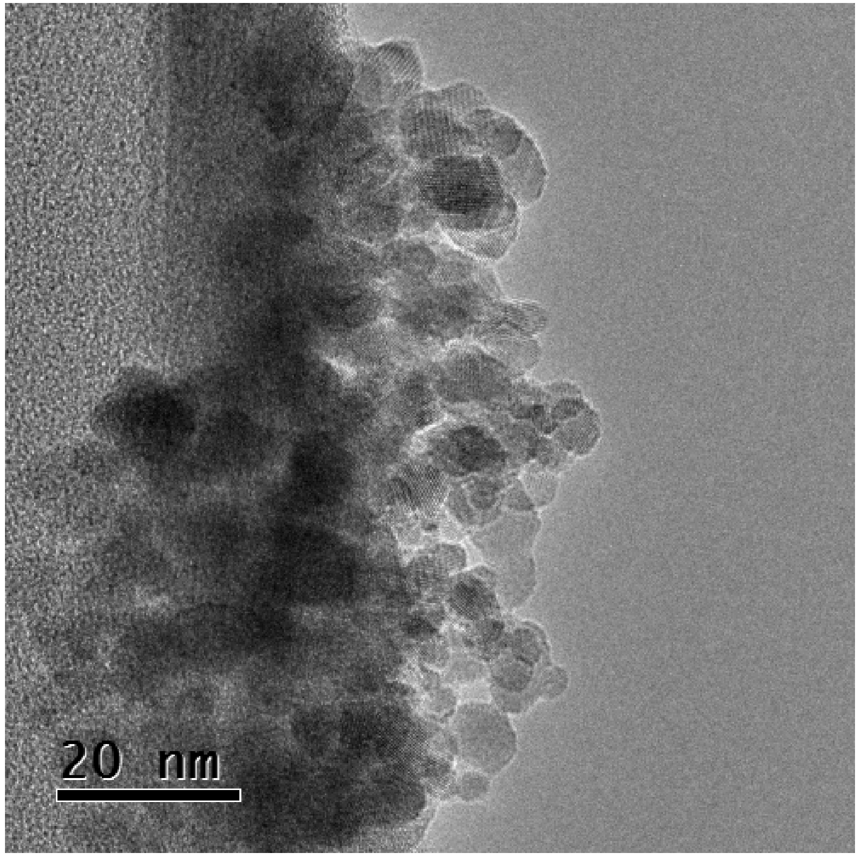
❑ Polyol and formic acid method

- ➢ Typical issues of catalyst particle agglomeration on support surface

Polyol method



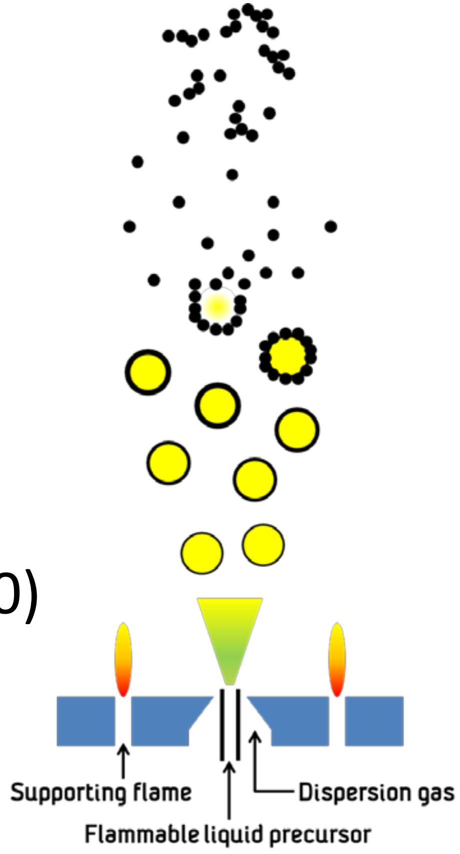
Formic acid method

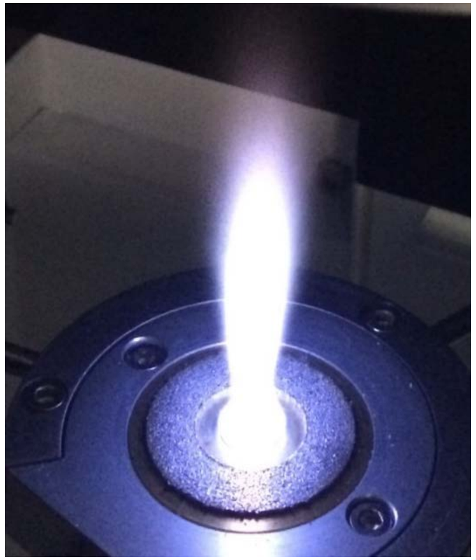


Pt catalyst deposition

❑ Flame spray pyrolysis (one-step synthesis)

- Support material: $Sn_{0.93}Sb_{0.07}O_2$
- Pt catalyst loading: 9-20 wt% Pt
- Solvent
  - Acetone - xylene (50-50 mixture)
- Precursors
  - Tin (II) 2-ethylhexanoate
  - Antimony (III) ethoxide
  - Platinum (II) acetylacetonate
- Operating conditions (Tethis NPS10)
  - Flame: 1.5 L/min CH_4 / 3.2 L/min O_2
  - Dispersion gas (O_2): 5 L/min
  - Liquid flow rate Flame: 5 mL/min





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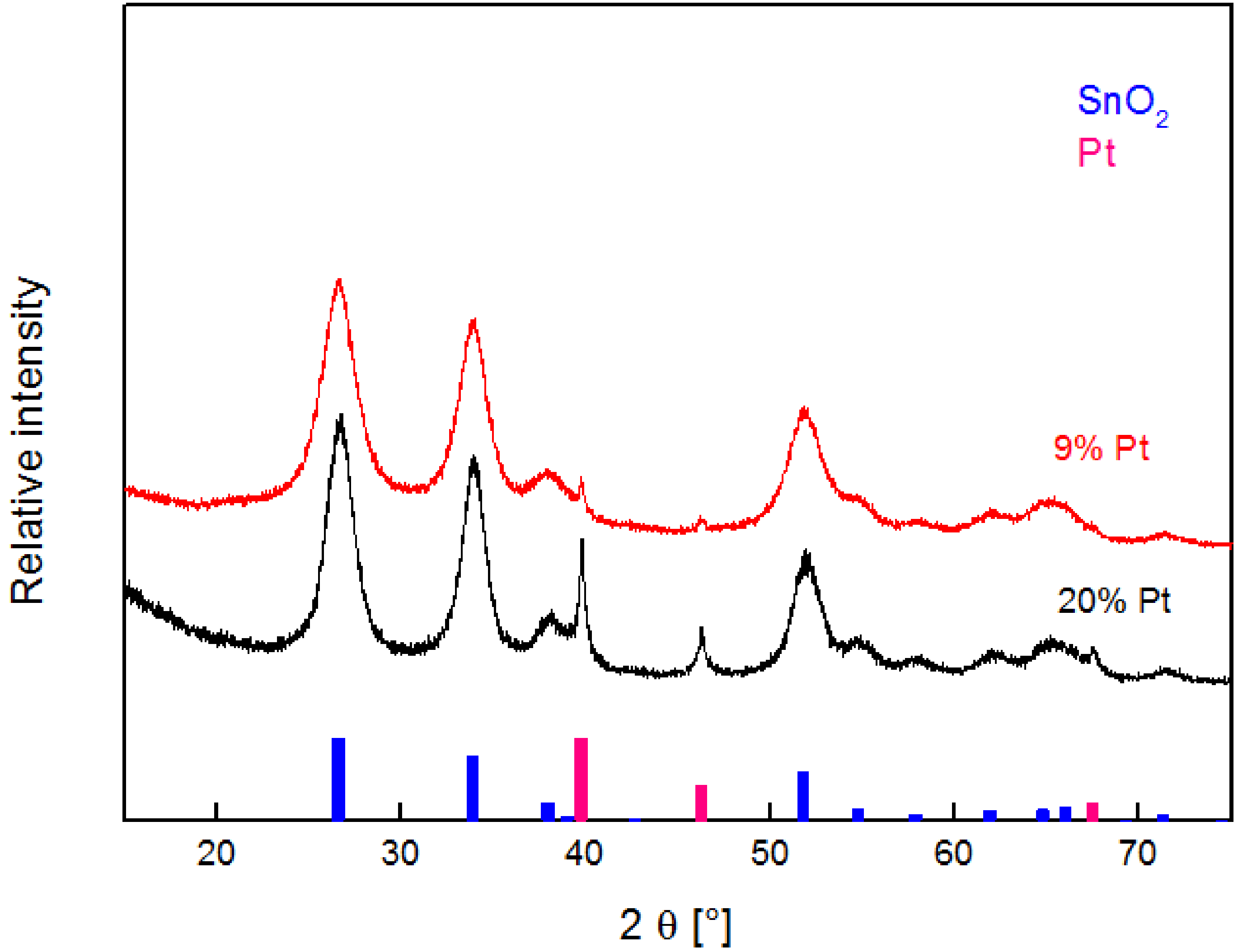
Pt catalyst deposition

❑ Flame spray pyrolysis (one-step synthesis)



- Example, $Sn_{0.93}Sb_{0.07}O_2$ + 9 wt% Pt
- XRD analysis indicate Pt particles is larger than support

Crystallite size

Pt: 30 nm

$Sn_{0.93}Sb_{0.07}O_2$: 5 nm

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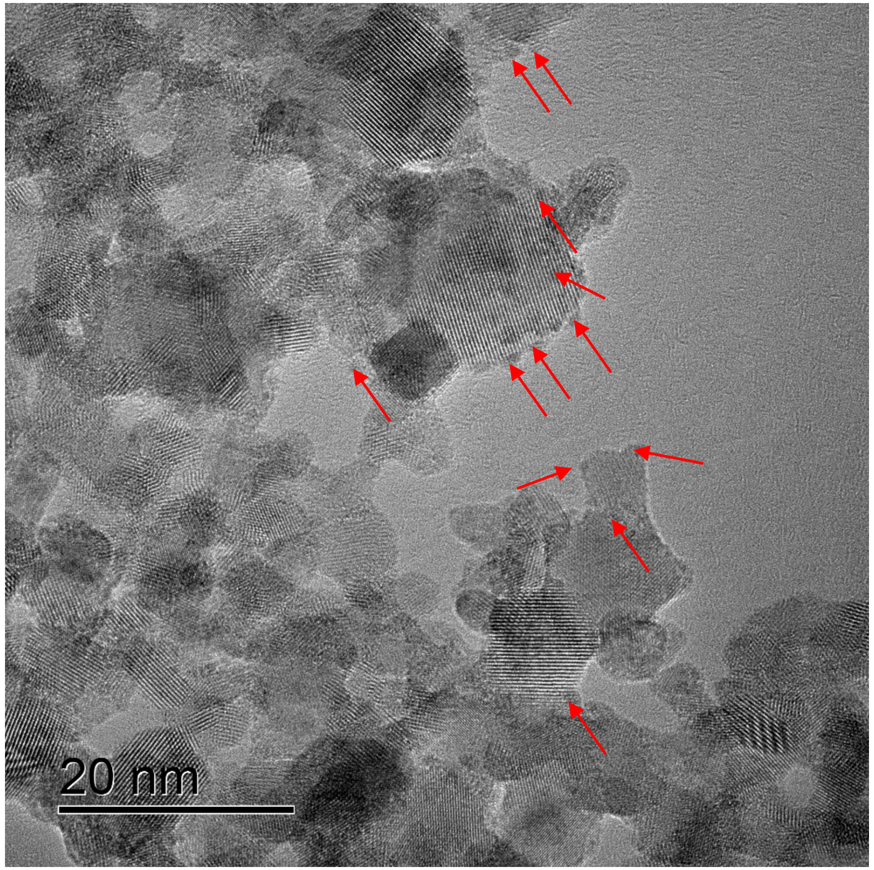
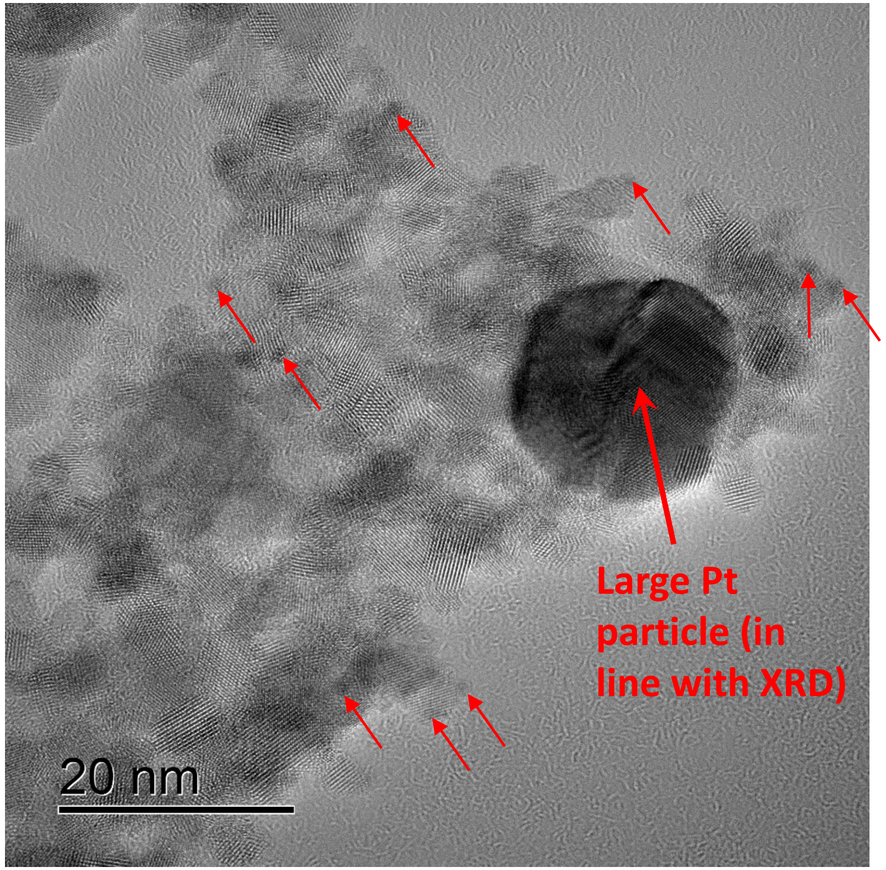
Pt catalyst deposition

❑ Flame spray pyrolysis (one-step synthesis)

➢ Example, $Sn_{0.93}Sb_{0.07}O_2$ + **9 wt% Pt**

➢ Interesting analysis by TEM (support: 3-30 nm, Pt: >20 nm + ~1nm particles)





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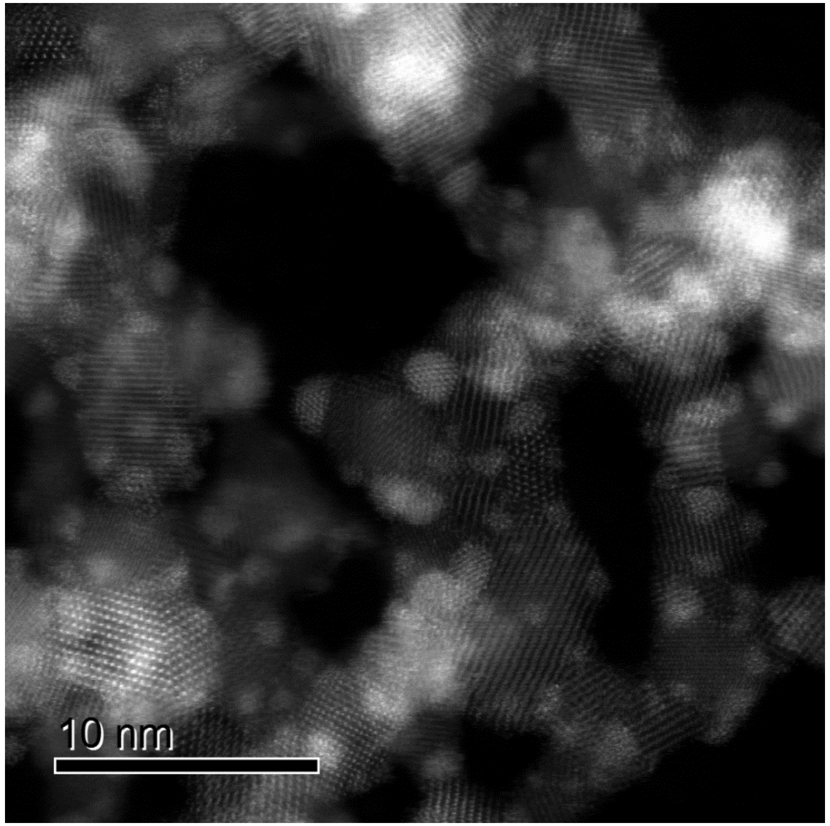
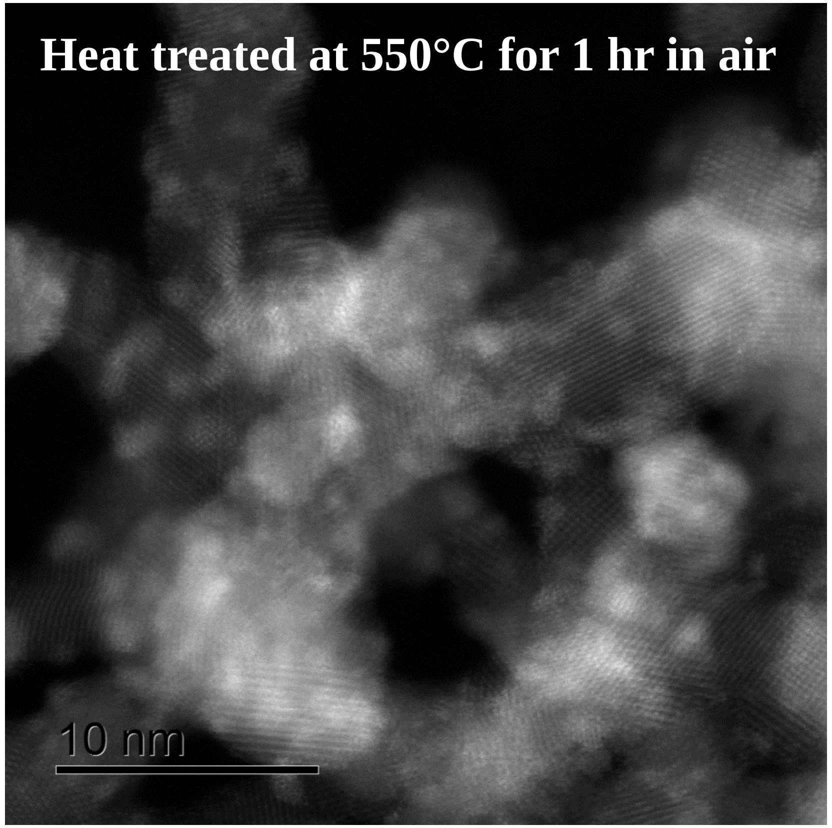
Pt catalyst deposition

❑ Flame spray pyrolysis (one-step synthesis)

- Example, $Sn_{0.93}Sb_{0.07}O_2$ + **20 wt% Pt**
- Similar with higher density of ~1 nm crystalline Pt particles (also some larger, 2-3 nm)





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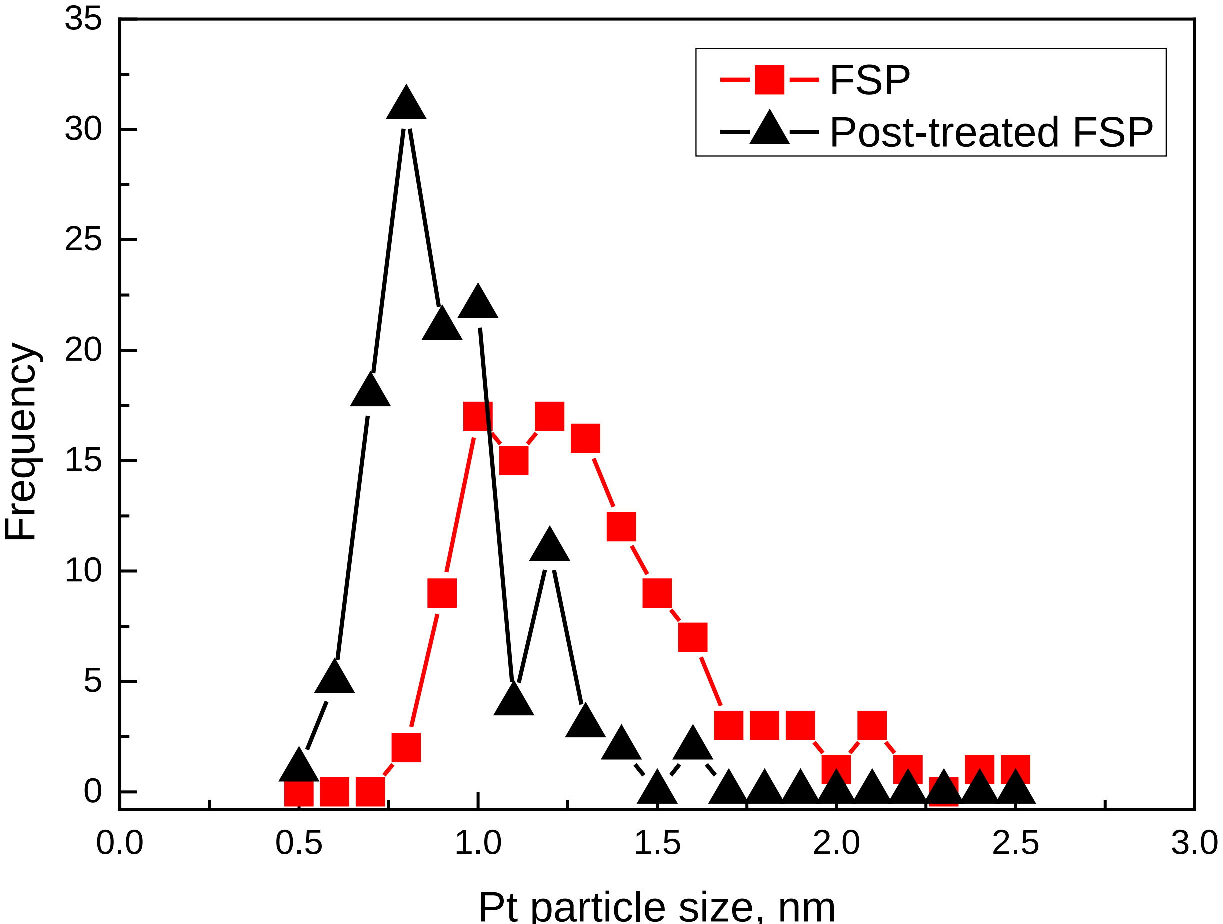
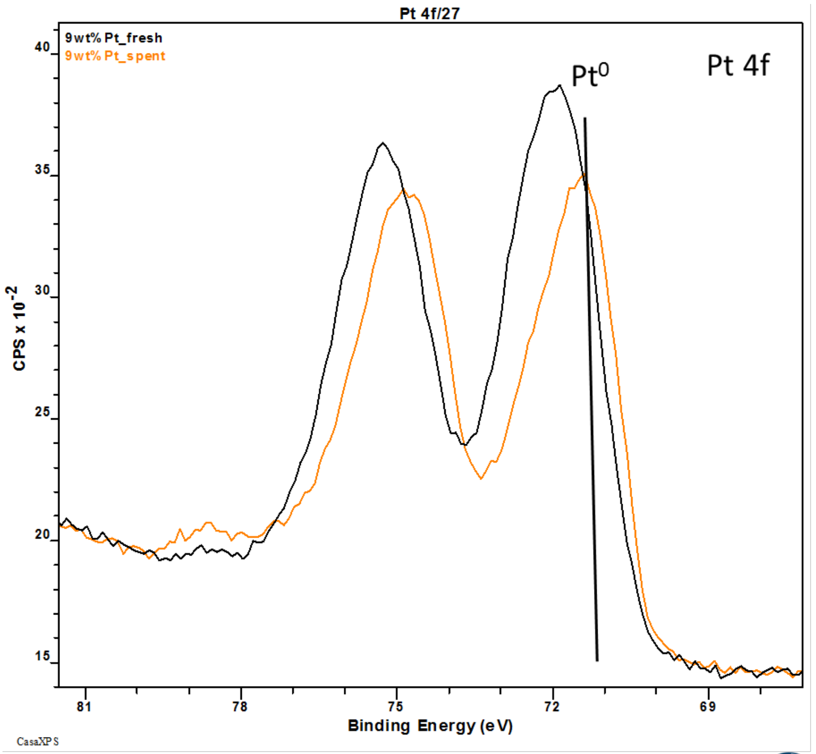
Pt catalyst deposition

- ❑ Flame spray pyrolysis (one-step synthesis)
  - ➢ Example, $Sn_{0.93}Sb_{0.07}O_2$ + **<u>20 wt% Pt</u>**
  - ➢ Slight reduction in size with heat treatment



- ➢ XPS indicates shift towards more metallic Pt → oxide layer on particles removed by post treatment?



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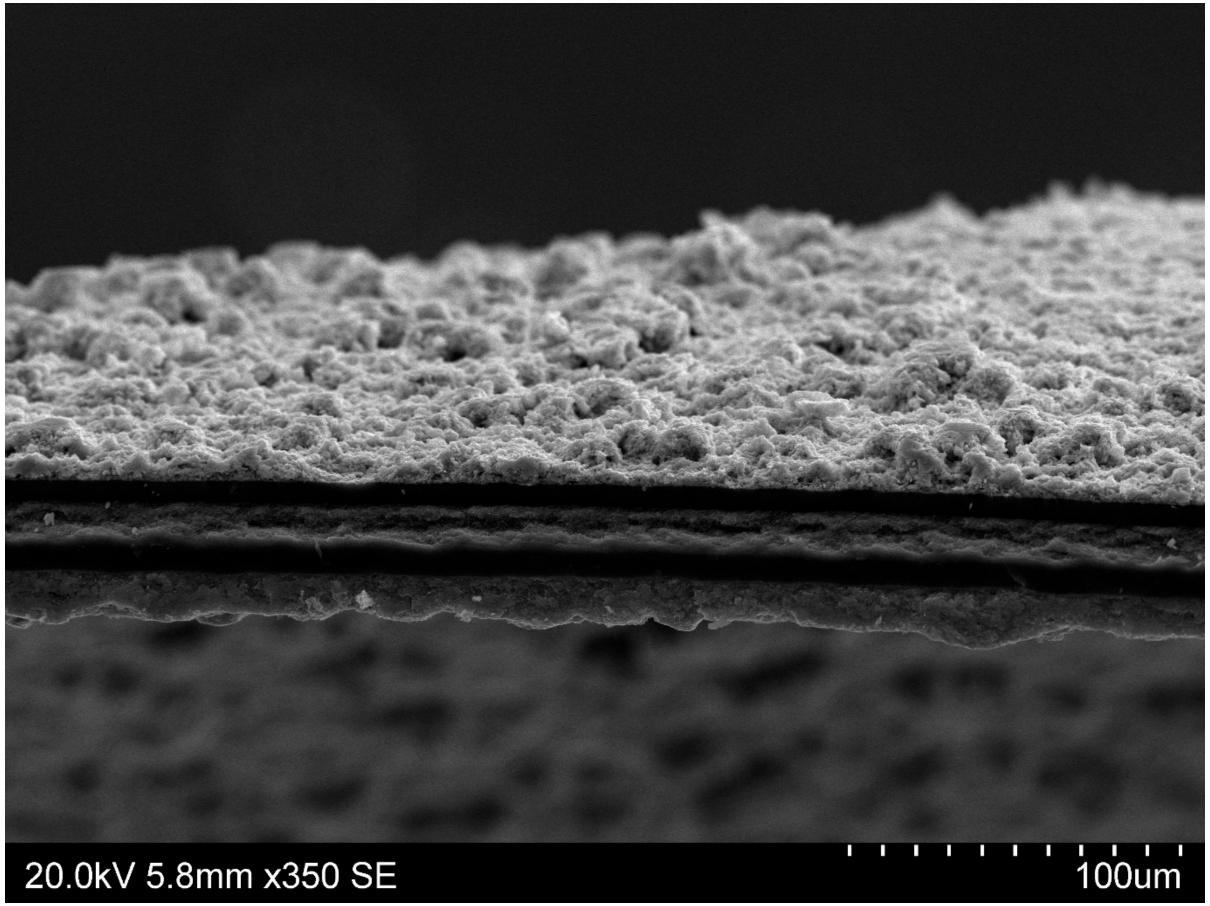
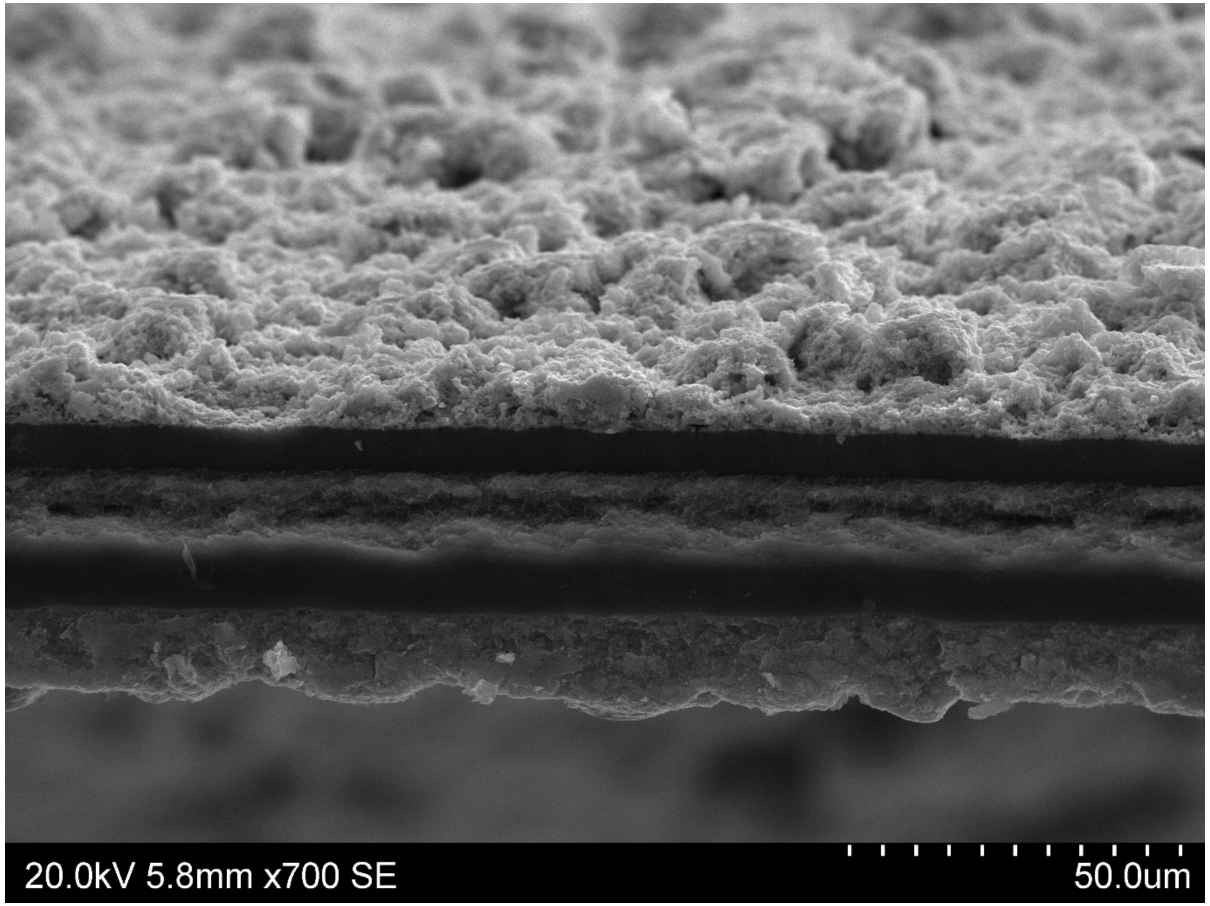
Electrode preparation

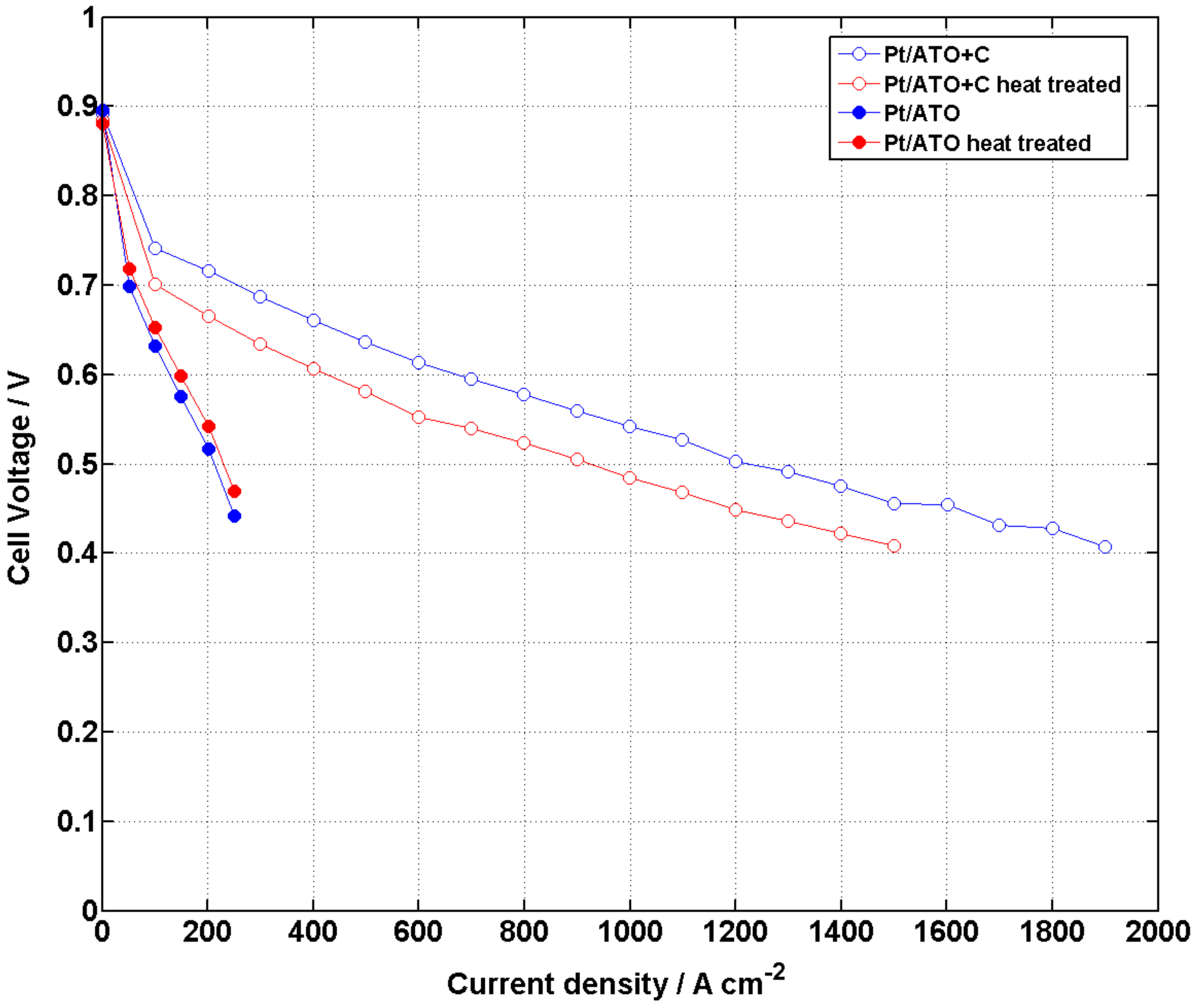
- Cathode: $Sn_{0.97}Sb_{0.03}O_2$ + 20 wt% Pt + ionomer (and 50 vol% C-mixtures)





Fuel cell testing

- $Sn_{0.97}Sb_{0.03}O_2$ + 20 wt% Pt
  - Poor performance
  - Post treated worse than as synthesized
  - Mixed with carbon (50:50 vol.%)
  - Better performance, reduced cell resistance.
  - Still more work to be done on electrode optimization



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Summary

- Flame spray pyrolysis optimal for supported Pt nanoparticles on oxide support material
  - Versatile technique with respect to complex oxide nanomaterials
  - Predictable microstructures
  - Down to 1 nm Pt nanoparticles can be obtained

- Some further optimizations required
  - Control of Pt-particle size distribution
  - Evaluation of reduced Pt content
  - Further development of electrodes

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The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement #325327 (SMARTCat project).

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