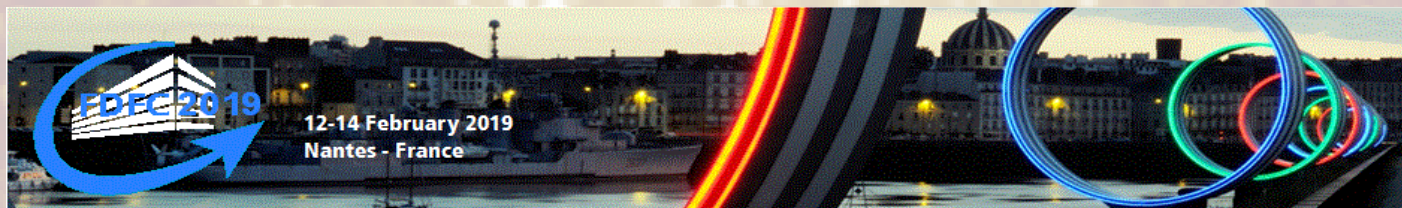


FDFC 2019

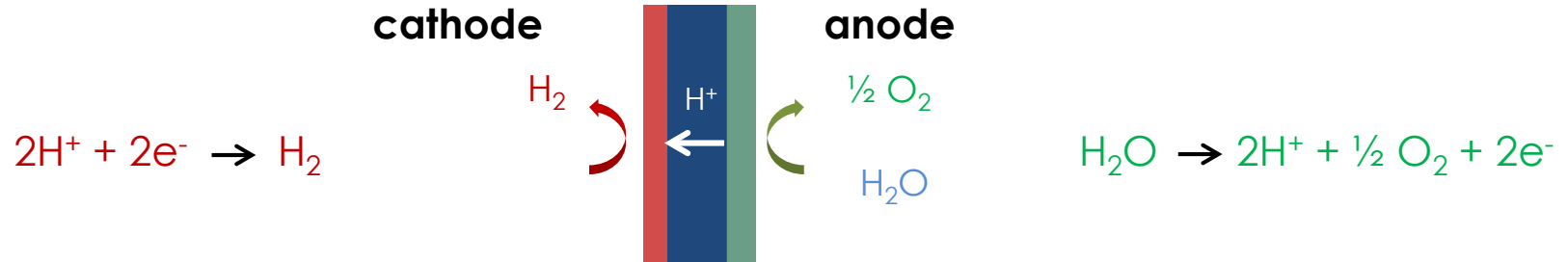
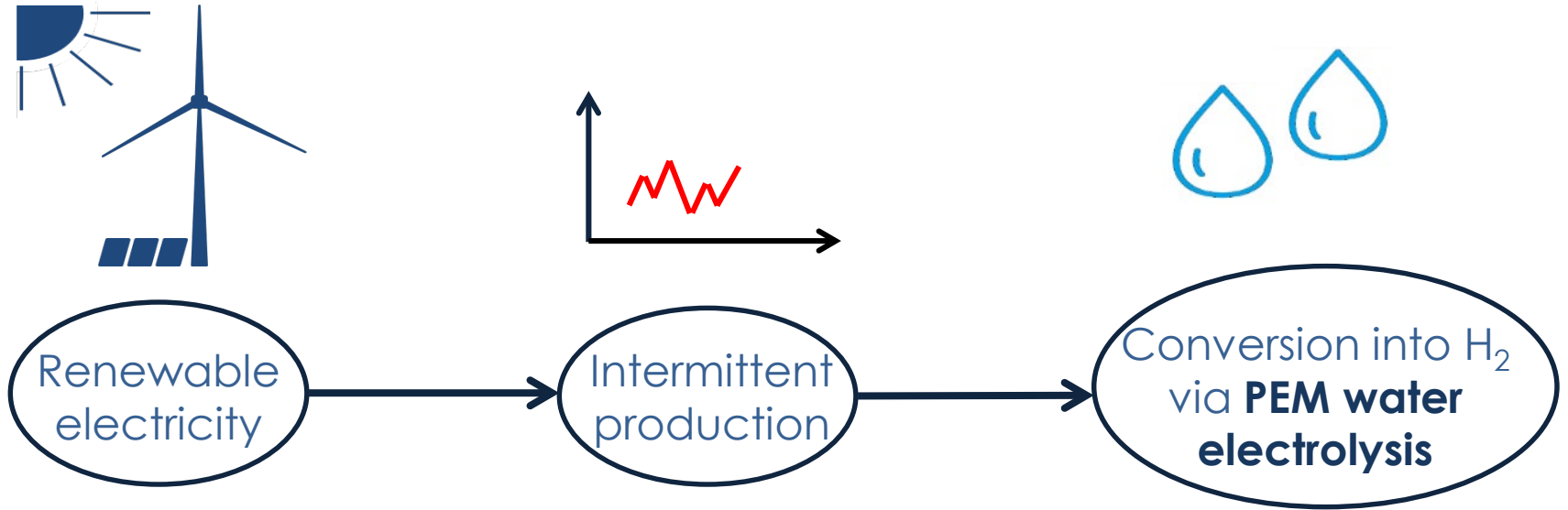
Oxygen Evolution Reaction Investigation on Model Catalysts in Acidic Medium: comparison between Ir(111), Ir(210) and nanostructured Ir(210)

M. Scohy¹, V. Martin¹, S. Abbou¹, E. Sibert¹, L. Dubau¹, B. Gilles², F. Maillard¹

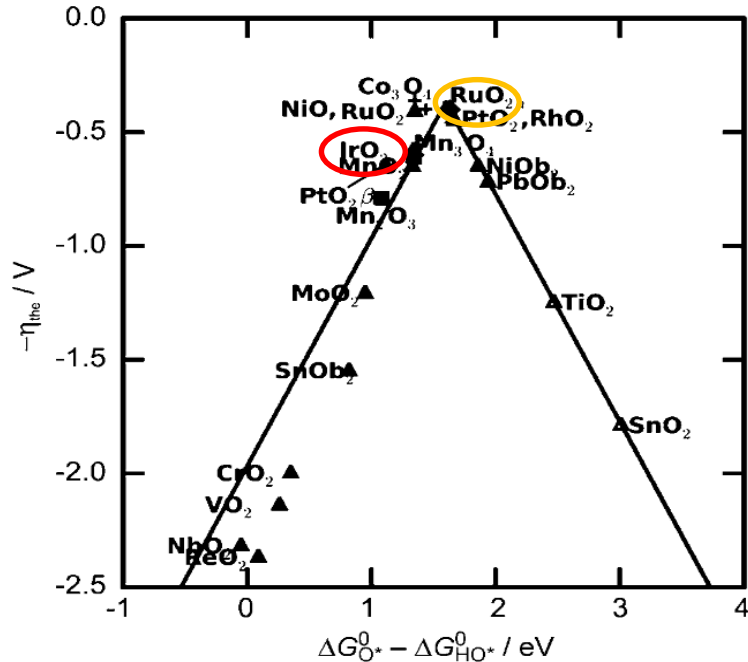
1. Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP*, LEPMI, 38000 Grenoble, France
* Institute of Engineering Univ. Grenoble Alpes
2. Univ. Grenoble Alpes, SIMAP, F-38000 Grenoble, France CNRS, SIMAP, F-38000 Grenoble, France



Context



Context

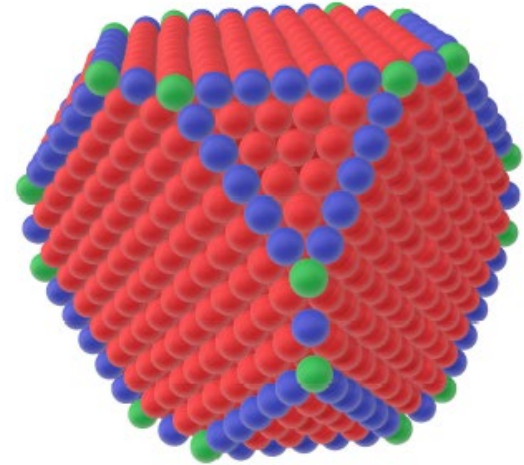


Man, I. C. *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. *ChemCatChem* **3**, 1159–1165 (2011).

- $\text{IrO}_2 \rightarrow$ best compromise between **activity** and **stability**
- **High cost** and **scarce** material
- Design of more **efficient** catalysts to increase the specific catalytic **activity**

Context

- Nanoparticles are composed of **facets**, **edges** and **kinks**
- Fundamental understanding of phenomena linked to the **electronic structure** of the electrode surface is necessary
- Study **single-crystal** surfaces



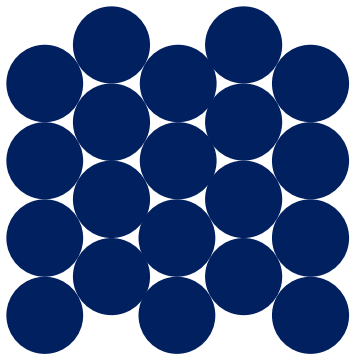
Context

- Study of 3 different surfaces
 - 3 « fresh » surfaces
 - 3 oxidized
 - **Initial characterizations**
 - Electrochemical characterizations
 - AFM
 - XPS
 - **Ageing via chronoamperometry**
 - ICP-MS measurement
 - **Final characterizations**
 - Electrochemical characterizations
 - AFM

Initial state - fresh surfaces

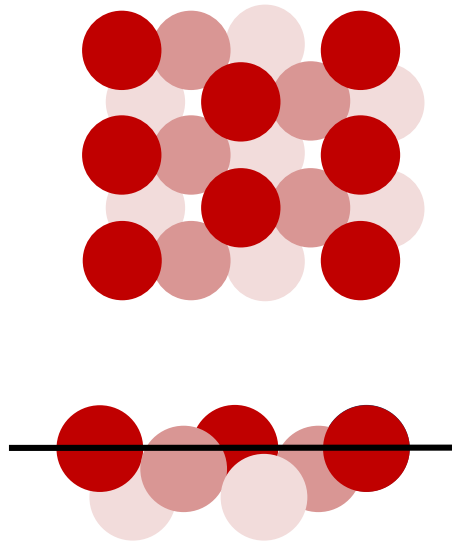
Ir(111)

most densely packed structure



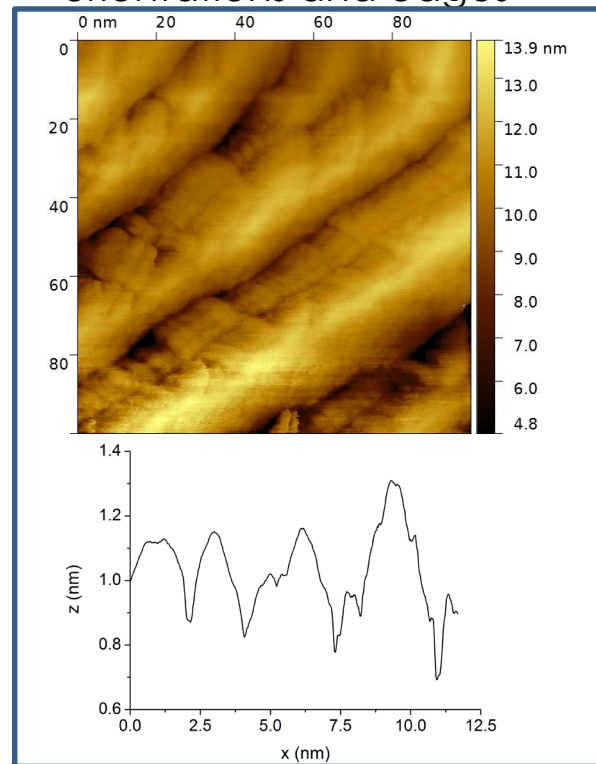
Ir(210)

open structure



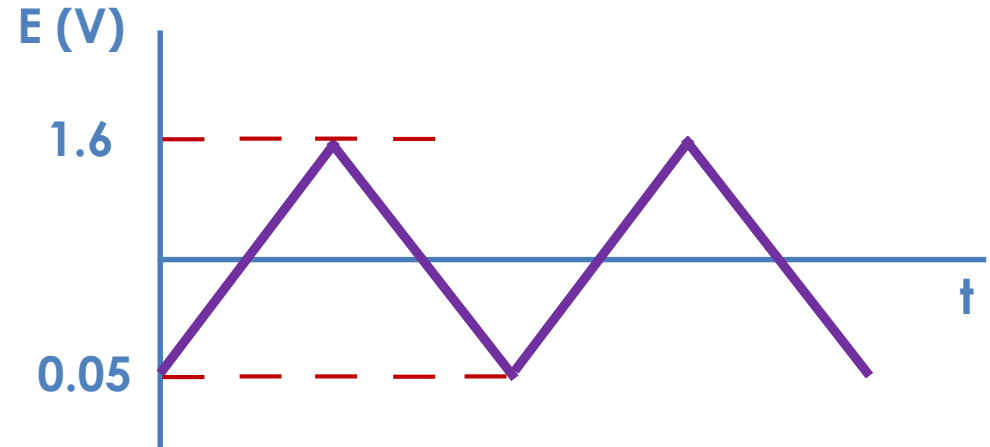
Nanostructured Ir(210)

reconstructed structure with different orientations and edges



Initial state - electrochemically oxidized surfaces

- **Electrochemical oxidation** of the fresh surfaces:
 - 15 potential cycles between 0.05 V vs. RHE to 1.6 V vs. RHE
- **More active** but **less stable** for the OER than metallic iridium and thermally formed oxide²

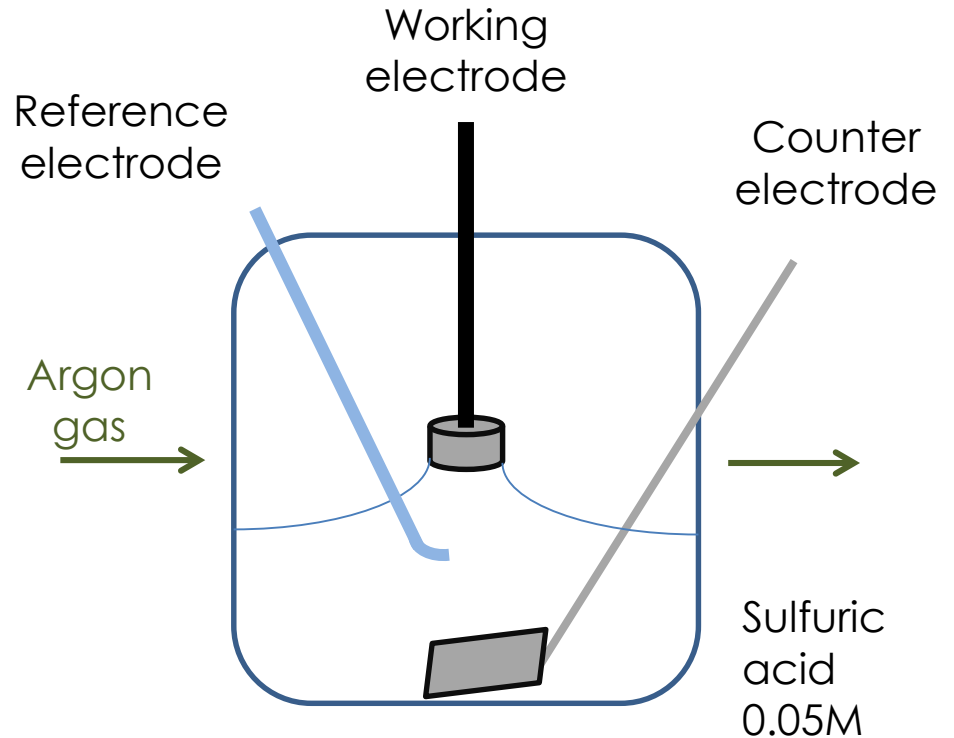


2. Cherevko, S., Geiger, S., Kasian, O., Mingers, A. & Mayrhofer, K. J. J. Oxygen evolution activity and stability of iridium in acidic media. Part 1. - Metallic iridium. *J. Electroanal. Chem.* (2016). doi:10.1016/j.jelechem.2016.04.033

Initial state - characterization

Electrochemical characterization

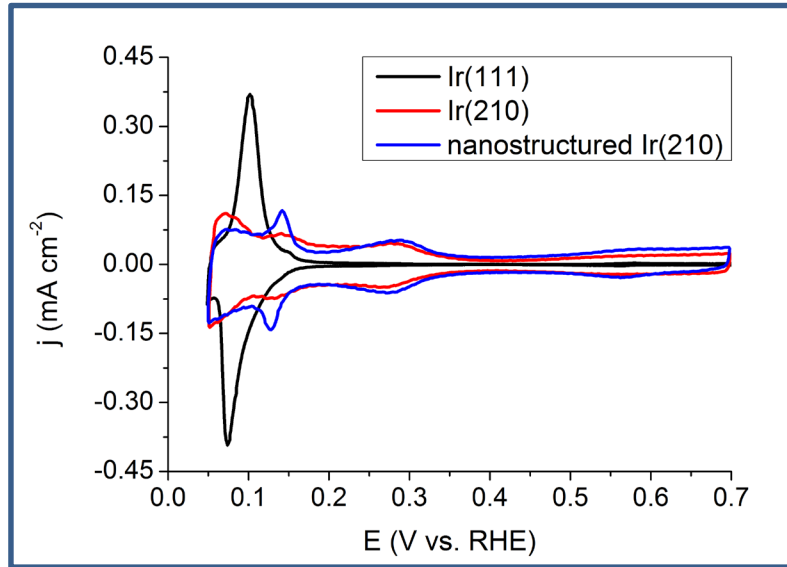
- Oxygen-hydrogen **flame annealing**
- Cooling into 5% H₂ + Ar mixture
- Protection by a droplet of ultrapure water
- **Hanging meniscus** configuration



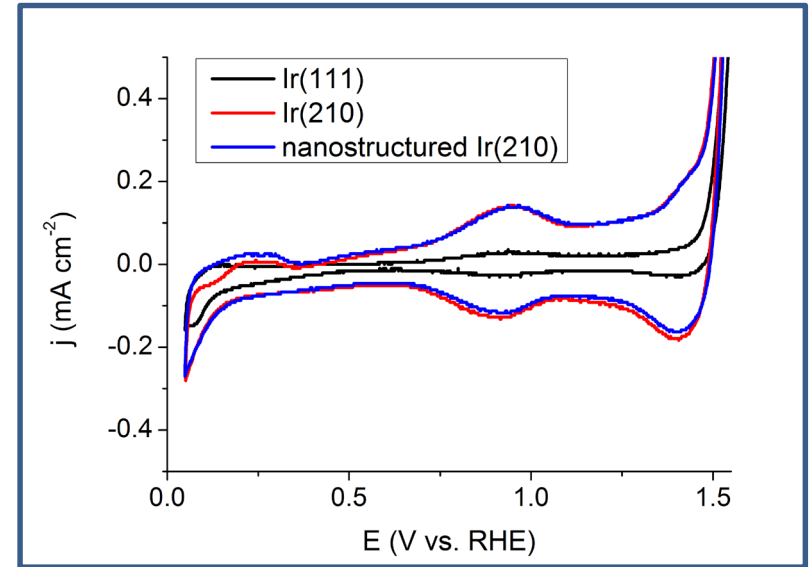
Initial state - characterization

Electrochemical characterization – cyclic voltammetry

Fresh surfaces



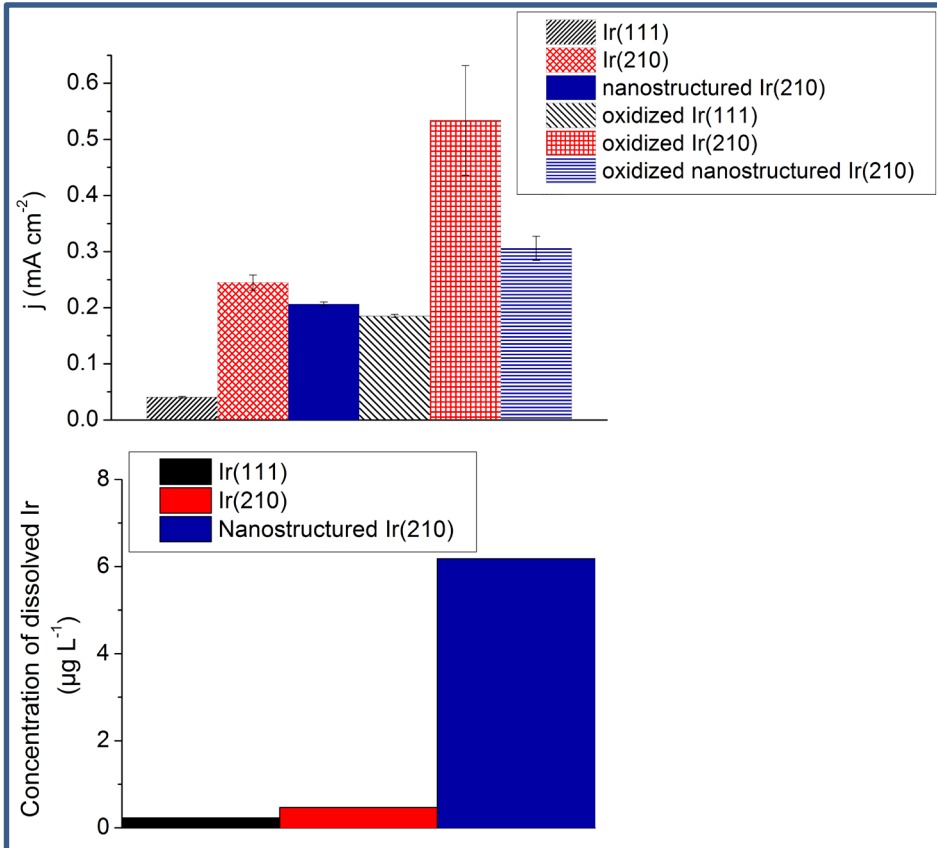
Oxidized surfaces



Sweep rate: 50 mV s⁻¹

Initial state - characterization

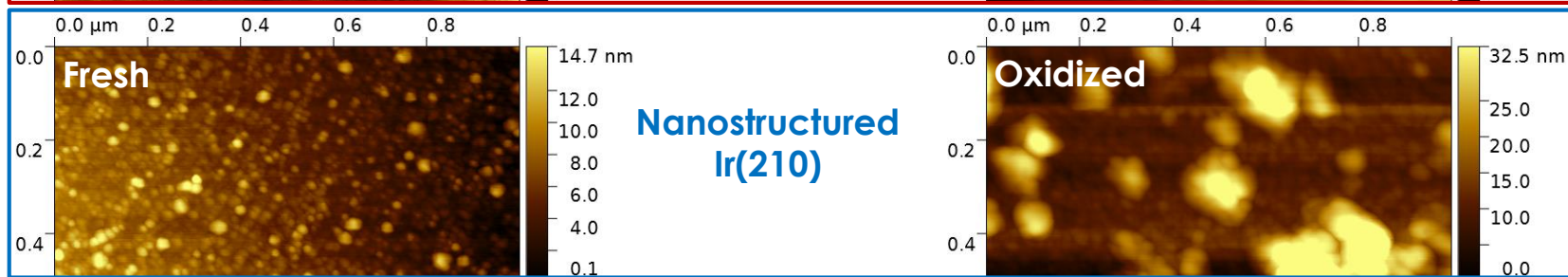
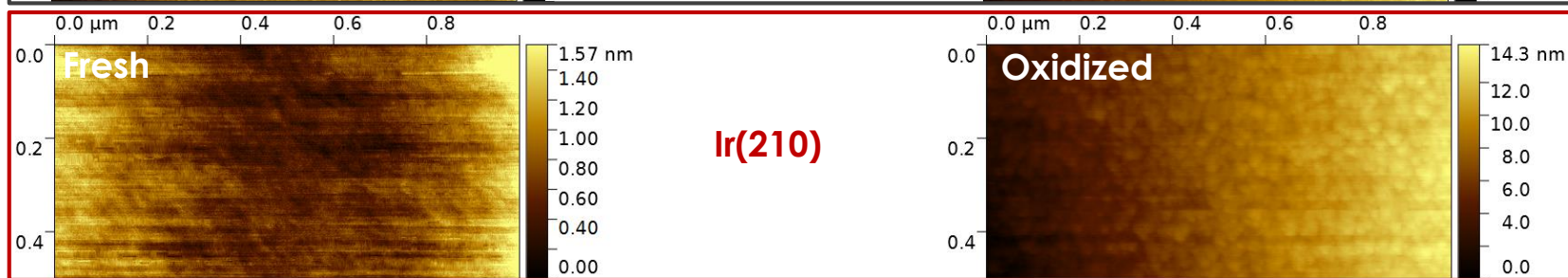
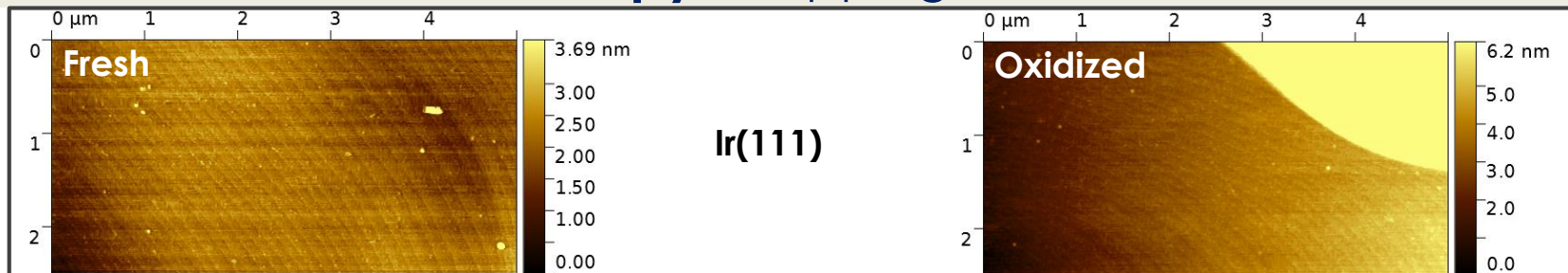
Electrochemical characterization – activity



- LSV at 5 mV s⁻¹ from 1.2 V vs. RHE to 1.6 V vs. RHE
- Current density at 1.51 V vs. RHE
- **Oxidized** surfaces are more **active**
- **(210)** is the most active
- Dissolution during oxidation: (111) < (210) < nanostructured (210)

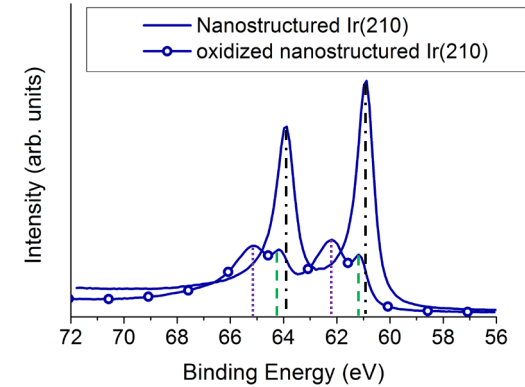
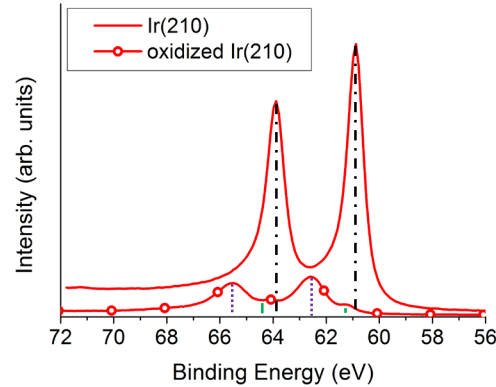
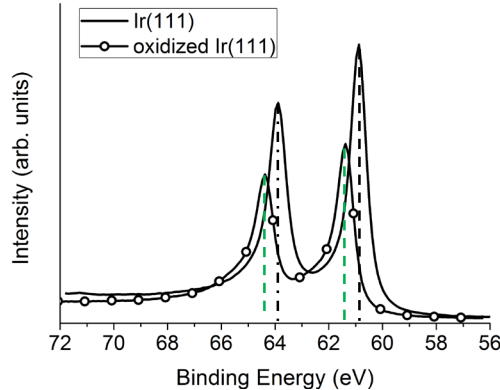
Initial state - characterization

Atomic Force Microscopy – tapping mode



Initial state - characterization

X-ray photoelectron spectroscopy



- After annealing and nanostructuring of 210: metallic Ir

Oxidized Ir(111):
Ir(IV)

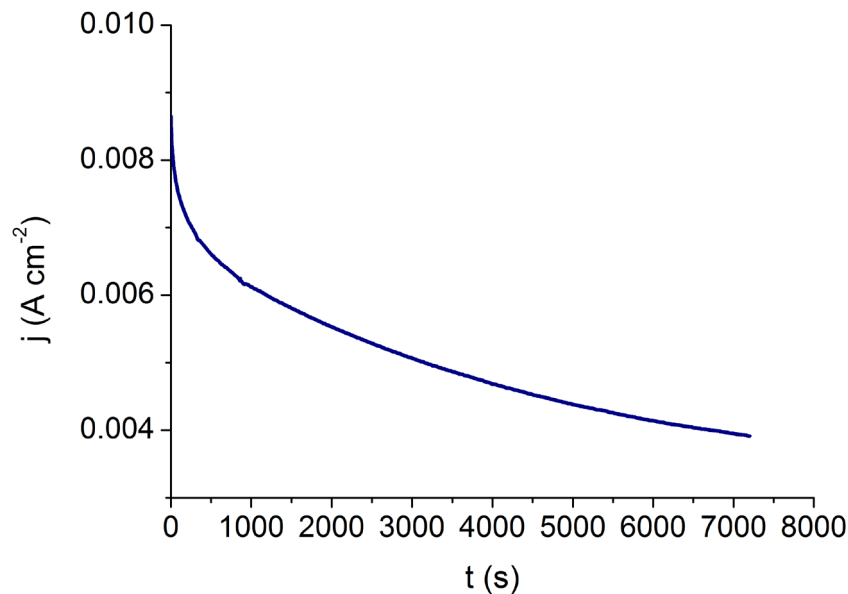
Oxidized Ir(210):
mixed **Ir(IV)/Ir(III)**

Oxidized
nanostructured Ir(210):
mixed **Ir(IV)/Ir(III)**

Ageing

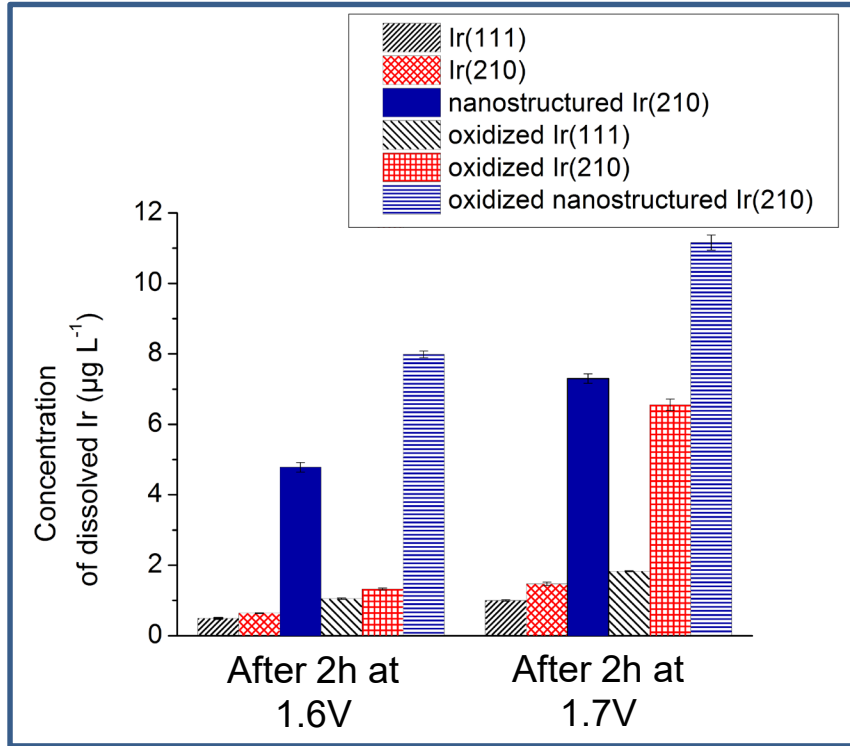
Electrochemical protocol

- Chronoamperometry
 - 2h at 1.6 V vs. RHE
 - 2h at 1.7 V vs. RHE
- Iridium content in the electrolyte analyzed by ICP-MS
- AFM images of the surfaces
- Measure of activity

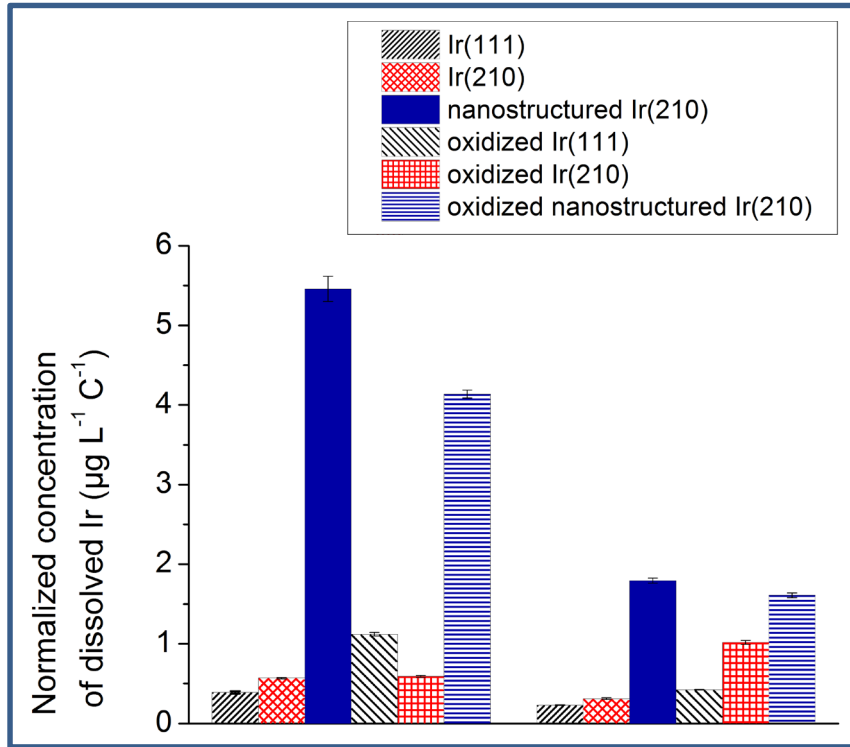


Ageing

ICP-MS



- Dissolution is more pronounced on nanostructured Ir(210)
- Higher dissolution for experiments at 1.7 V
- Oxidized surfaces dissolution is higher



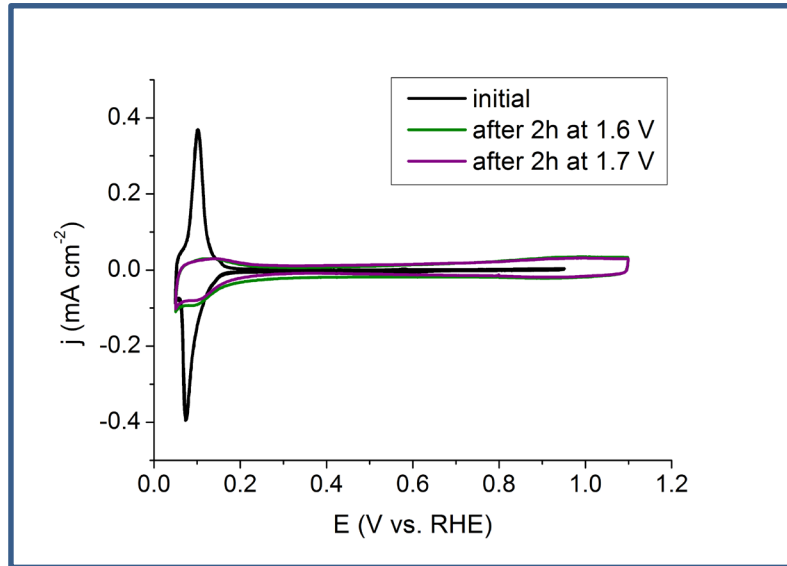
- If we normalized:
more dissolution on
nanostructured Ir(210)
especially at 1.6V

Final state - characterization

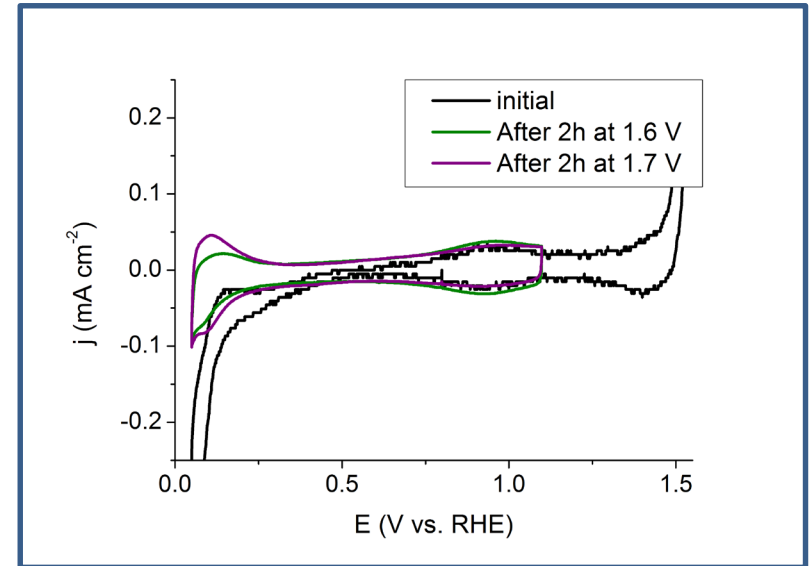
Electrochemical characterization – cyclic voltammetry

- Ir(111) and oxidized Ir(111)

Fresh surfaces



Oxidized surfaces



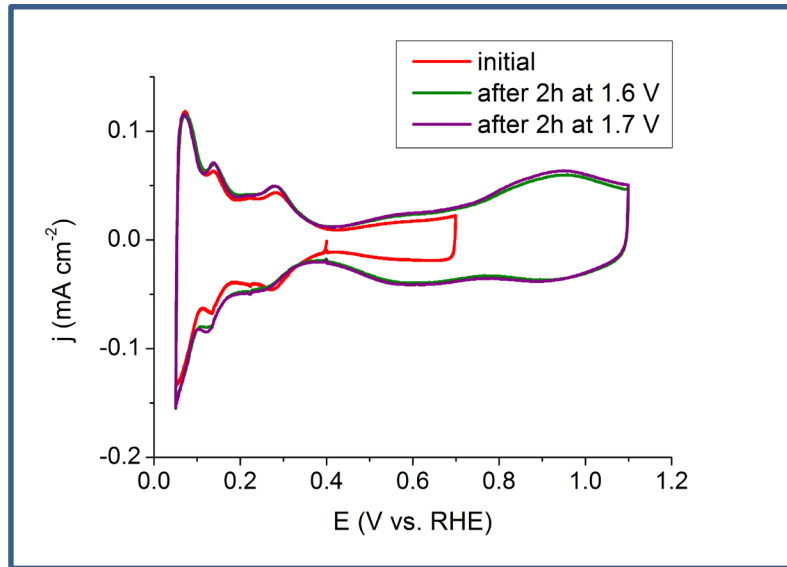
Sweep rate: 50 mV s⁻¹

Final state - characterization

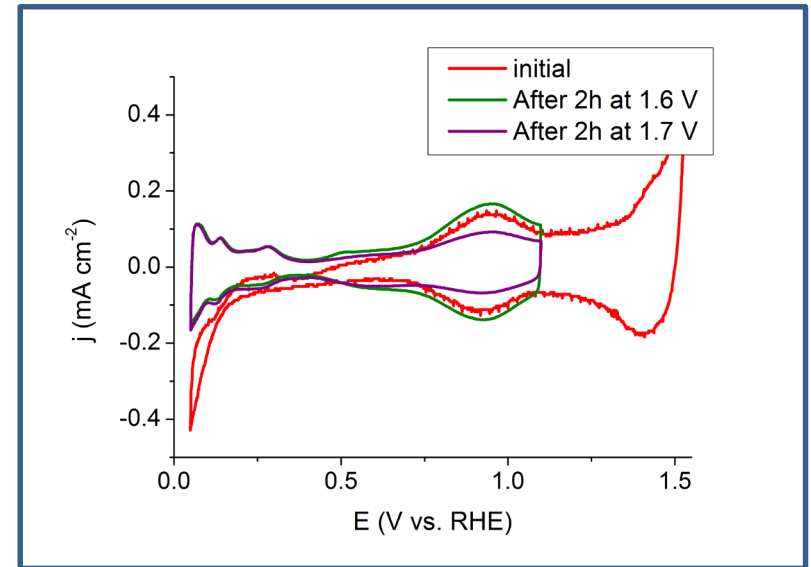
Electrochemical characterization – cyclic voltammetry

- Ir(210) and oxidized Ir(210)

Fresh surfaces



Oxidized surfaces



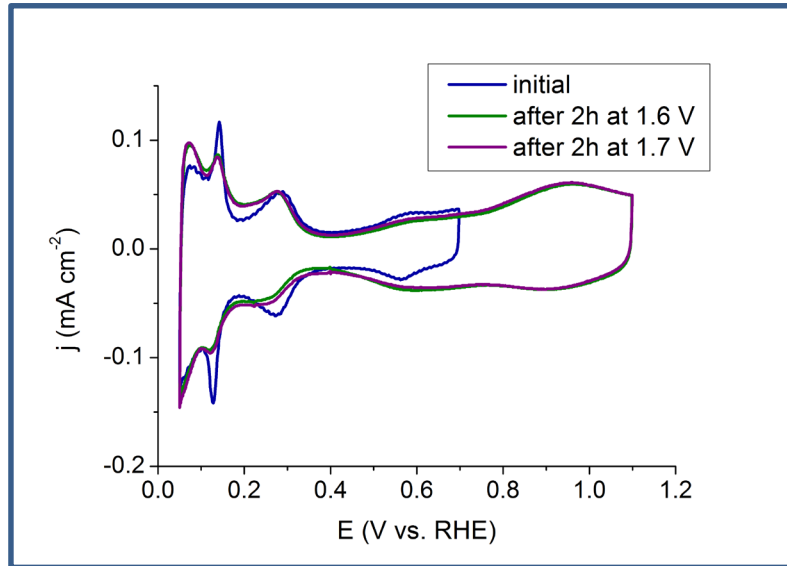
Sweep rate: 50 mV s⁻¹

Final state - characterization

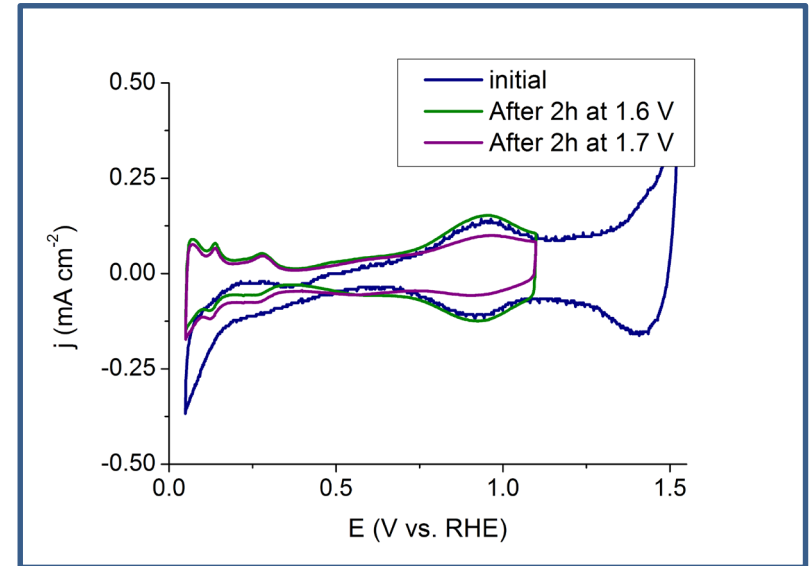
Electrochemical characterization – cyclic voltammetry

- Nanostructured Ir(210) and oxidized nanostructured Ir(210)

Fresh surfaces



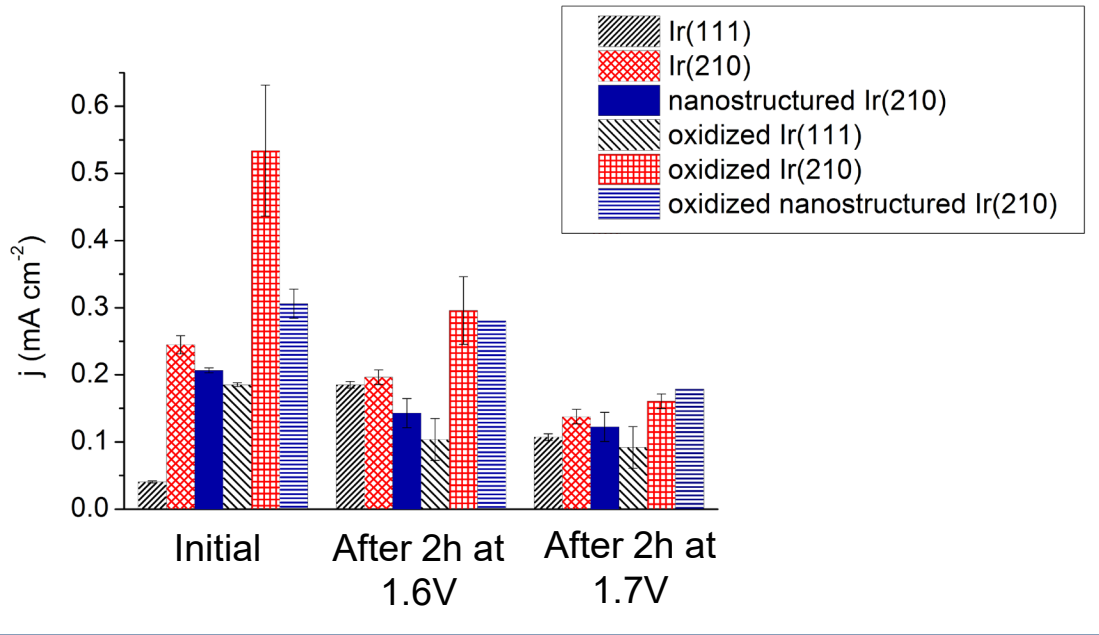
Oxidized surfaces



Sweep rate: 50 mV s⁻¹

Final state - characterization

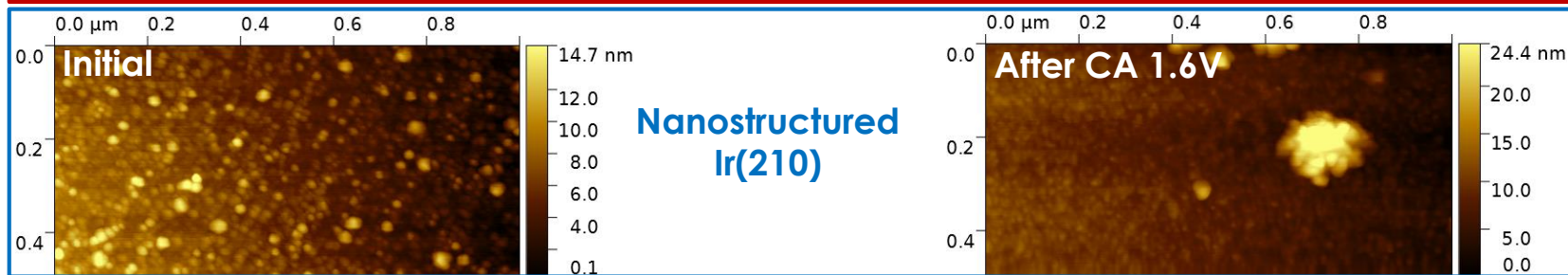
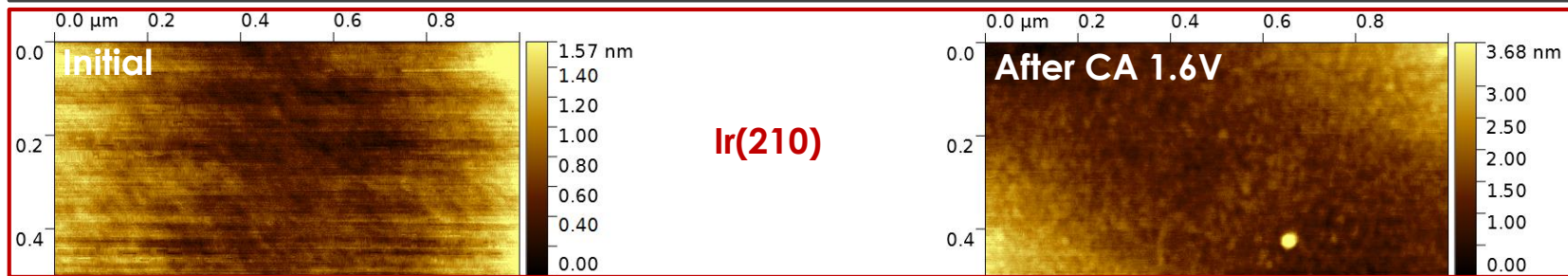
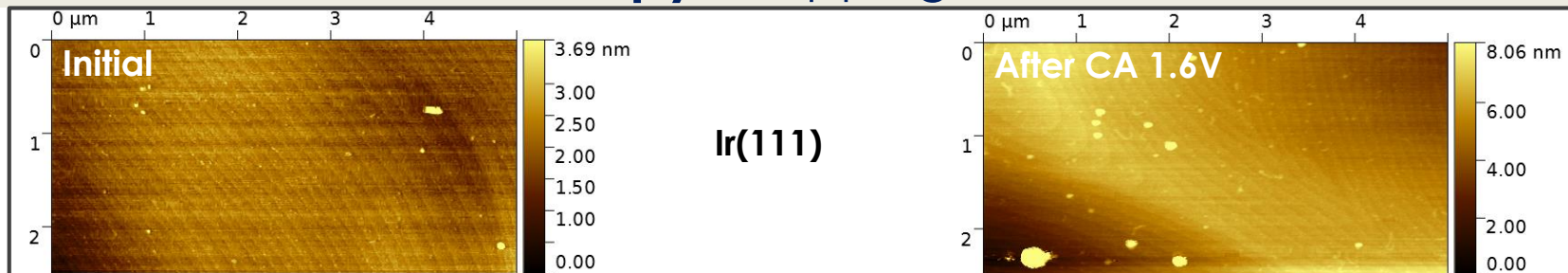
Electrochemical characterization – activity



- Current density at 1.51 V vs. RHE
- **Oxidized** surfaces are more **active** **except 111**
- After 2h at 1.7V, activities of the catalysts **tend to the same value**

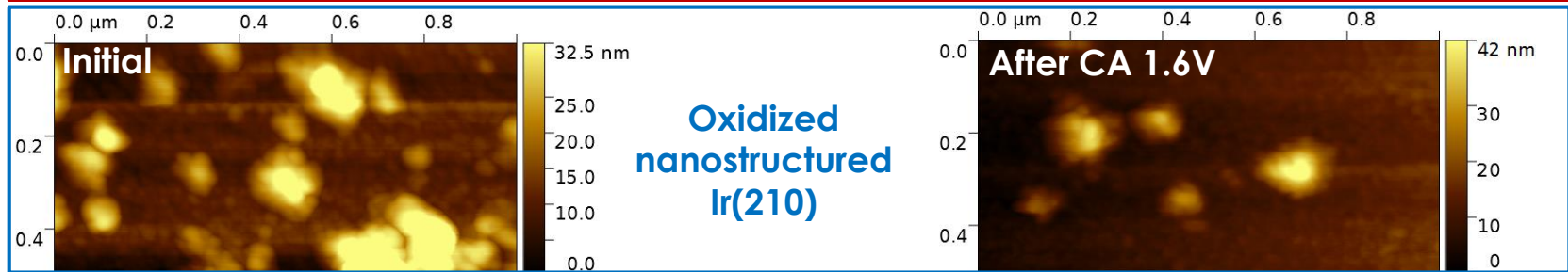
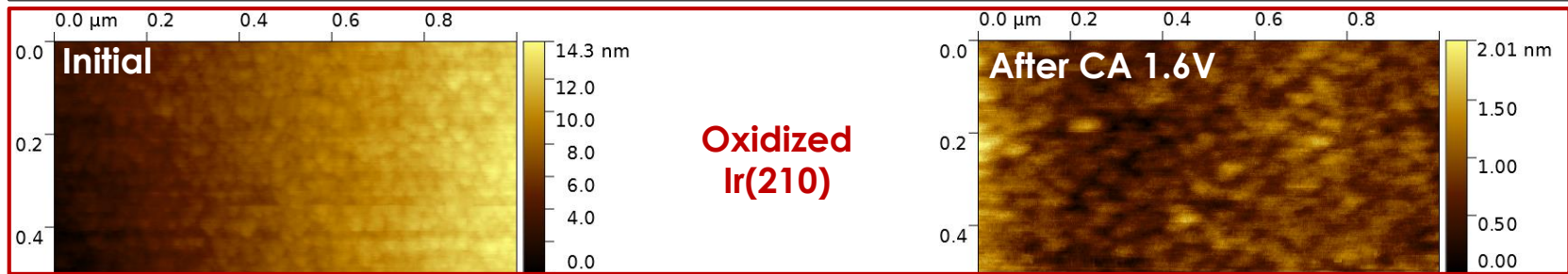
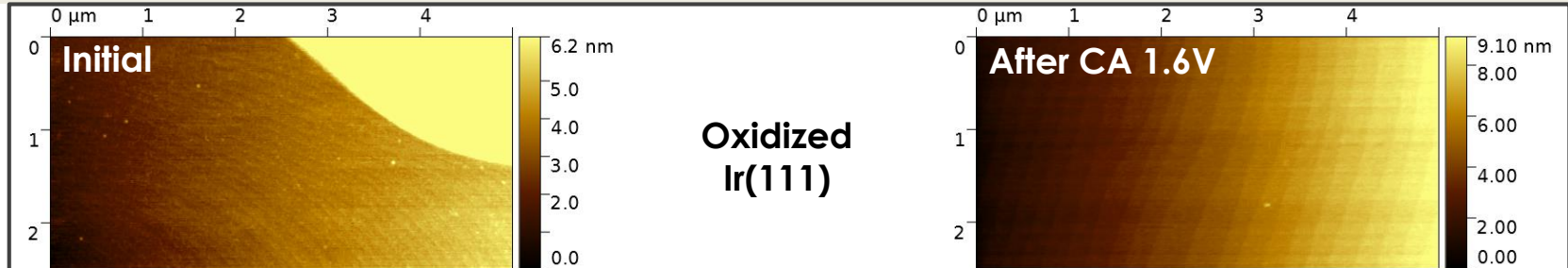
Final state - characterization

Atomic Force Microscopy – tapping mode



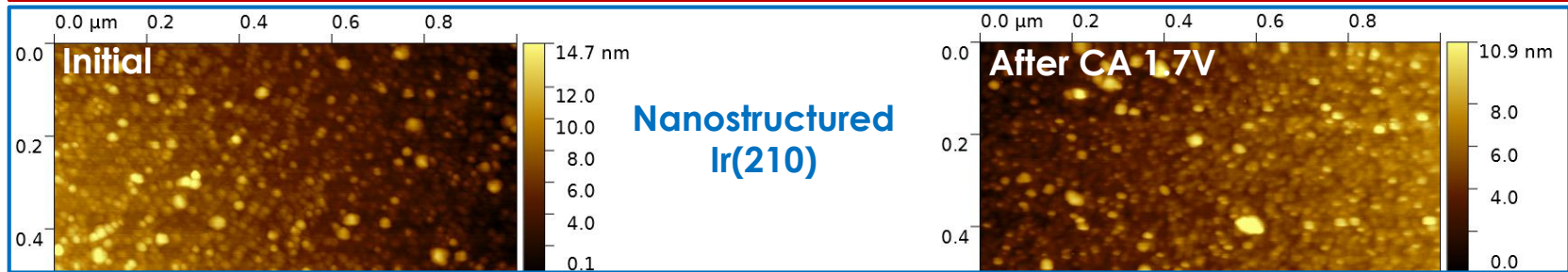
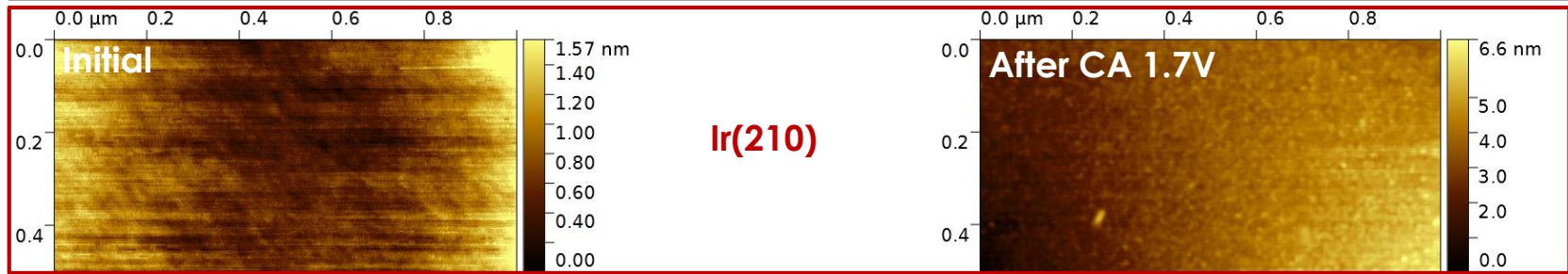
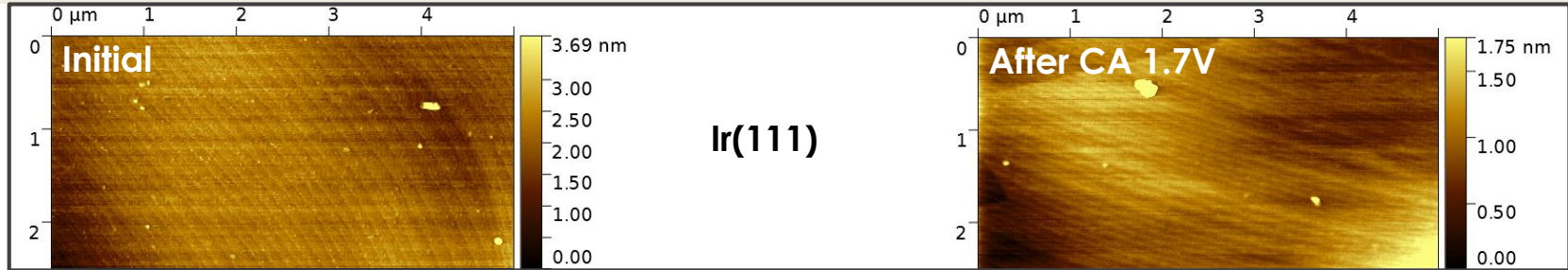
Final state - characterization

Atomic Force Microscopy – tapping mode



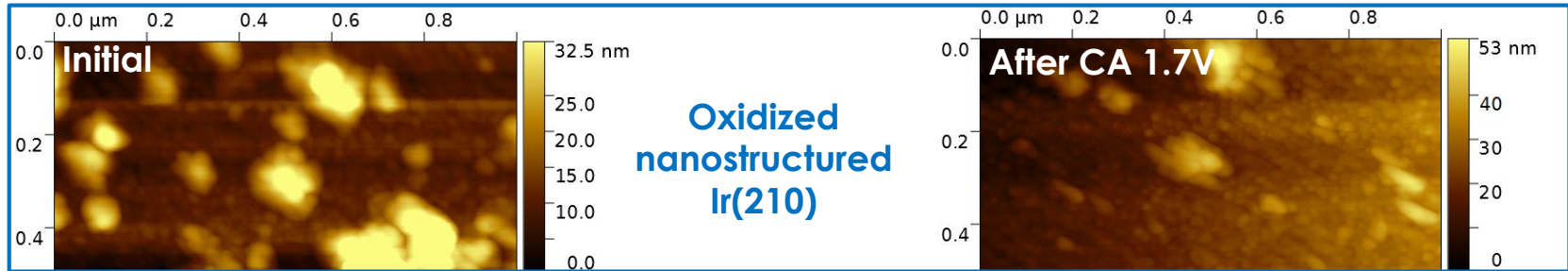
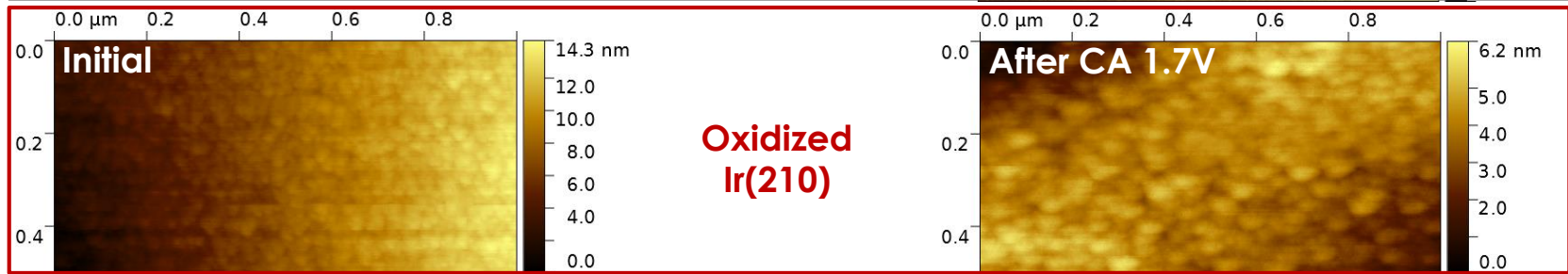
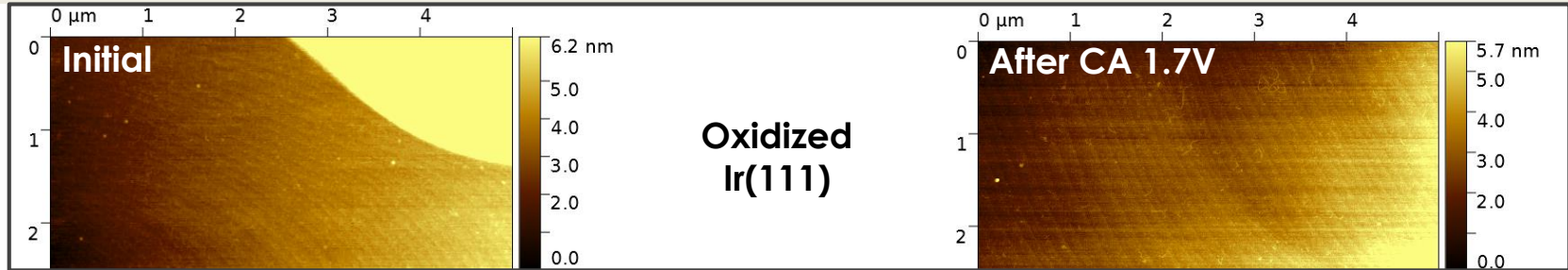
Final state - characterization

Atomic Force Microscopy – tapping mode



Final state - characterization

Atomic Force Microscopy – tapping mode



Comparison

| Ir(111) | Ir(210) | Nanostructured Ir(210) |
|---|--|---|
| Few defects | Small steps and edges | Steps, edges and planar surfaces |
| Oxide growth: Ir(IV) small oxide peak low dissolution rate | Oxide growth: Ir(IV)/Ir(III) higher oxide peak higher dissolution rate changes in surface morphology | Oxide growth: Ir(IV)/Ir(III) higher oxide peak very high dissolution rate changes in surface morphology |
| small activity higher for the oxide | high activity higher for the oxide | high activity higher for the oxide |
| Ageing: low dissolution rate increase of activity for fresh surface no major changes in surface morphology | Ageing: higher dissolution rate decrease of activity but still the highest changes in surface morphology | Ageing: highest dissolution rate activity quite comparable changes in surface morphology |

Conclusion

- Surfaces with **few defects** (Ir(111)) are the **least active** for OER
- **Electrochemically grown oxide** is more active than metallic surface, dissolution during the OER is comparable to metallic surfaces
- After ageing, activities are quite similar for all the surfaces
- Amount of Ir(III) seems to impact the activity of OER
- Surface morphology appears to impact mainly dissolution

Thank you for your attention !