Electrocatalytic Nanomaterials for Renewable Energy Storage

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EuroNanoForum 2019, Bucharest, June 12th 2019

outline

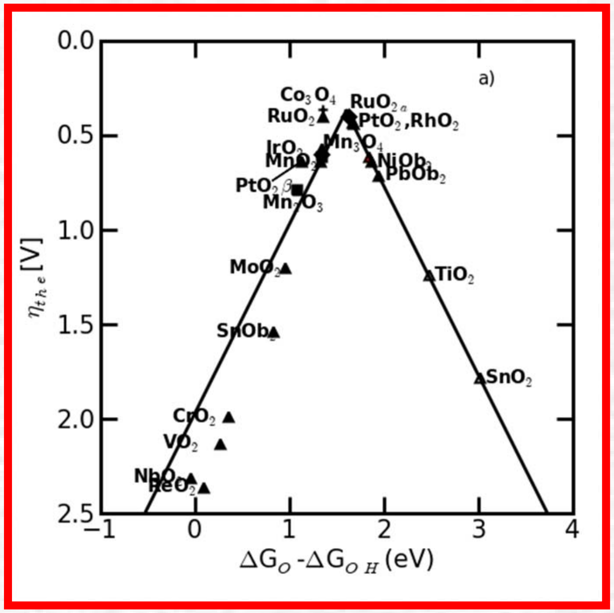
- **Bottleneck reactions management**
  - **Oxygen evolution**
    - **Rational design**
      - **Making the catalyst**
      - **Controlling the activity**
      - **Controlling the stability**
      - **Implementation issues**
- **Materials for energy storage - a way forward**

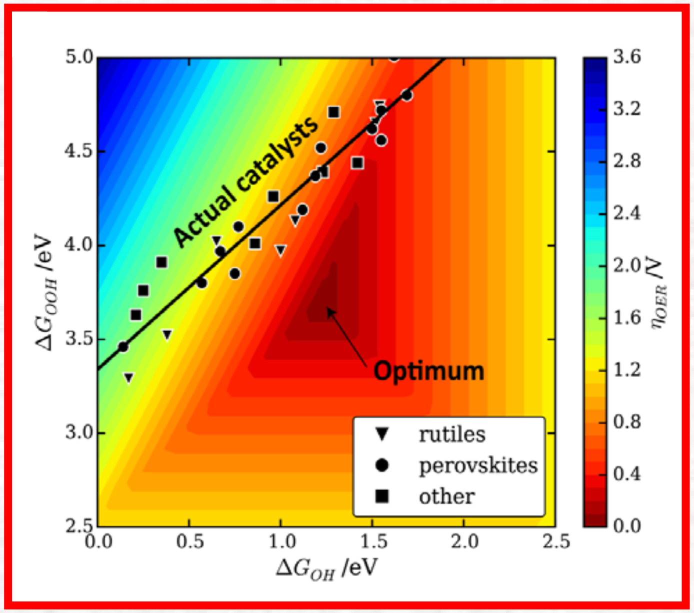
Hydrogen economy

$$H_2 + {}^{1}/_{2}\,O_2 \rightleftharpoons H_2O$$

$$S + H_2O \longrightarrow S-OH + H^+ + e^- \quad (1)$$
$$S-OH \longrightarrow S-O + H^+ + e^- \quad (2)$$
$$S-O + H_2O \longrightarrow SOOH + H^+ + e^- \quad (3)$$
$$S-OOH \longrightarrow S + O_2 + H^+ + e^- \quad (4)$$

$$S + H_3O^+ + e^- \longrightarrow S-H + H_2O \quad (1)$$
$$S-H + H_3O^+ + e^- \longrightarrow S + H_2 + H_2O \quad (2)$$
$$S-H + S-H \longrightarrow 2S + H_2 \quad (3)$$

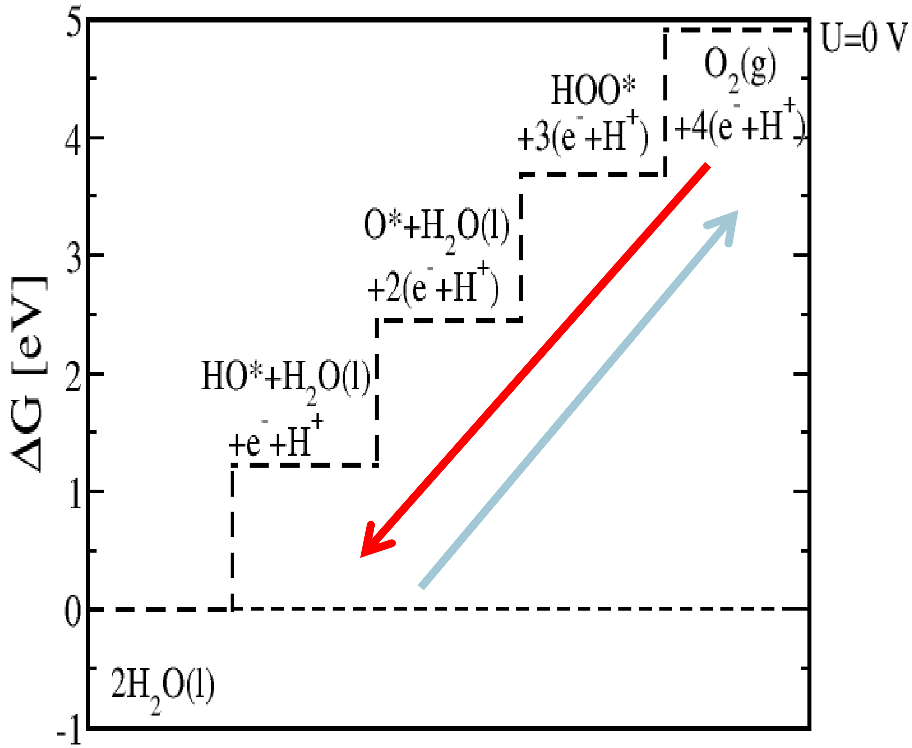




Water electrolysis is controlled by oxygen evolution!

OER catalysis limitations

Electrocatalysis of oxygen

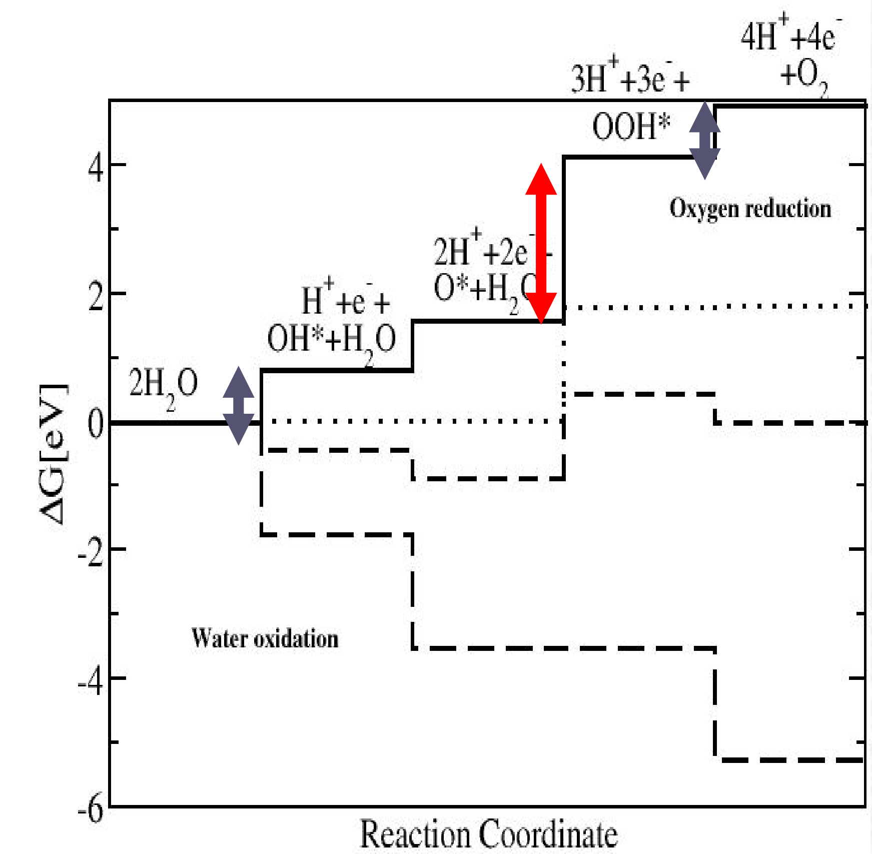


Sequence of 4 consecutive one electron oxidation steps

$\Delta G_1 \rightarrow \Delta G_2 \rightarrow \Delta G_3 \rightarrow \Delta G_4$

Each step has to be thermodynamically spontaneous!

U_{ORR} and U_{OER}

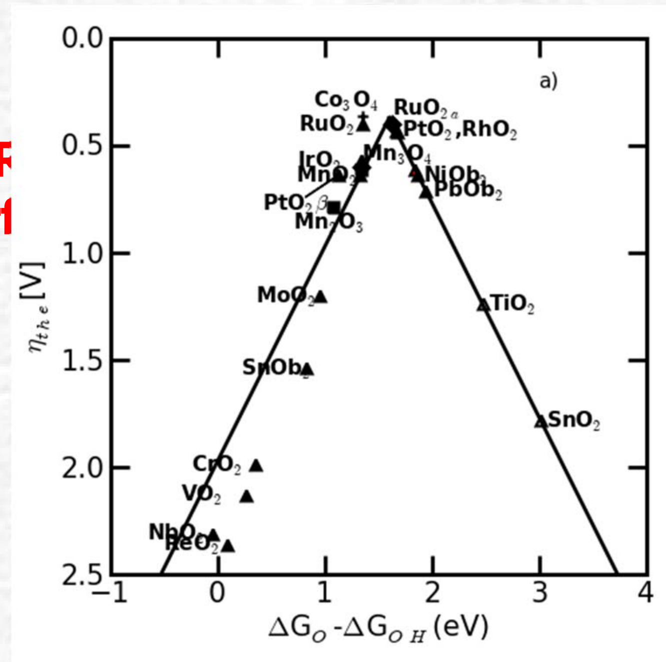


$\Delta G_1 \rightarrow \Delta G_2 \rightarrow \Delta G_3 \rightarrow \Delta G_4$

$U_{OER}=\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

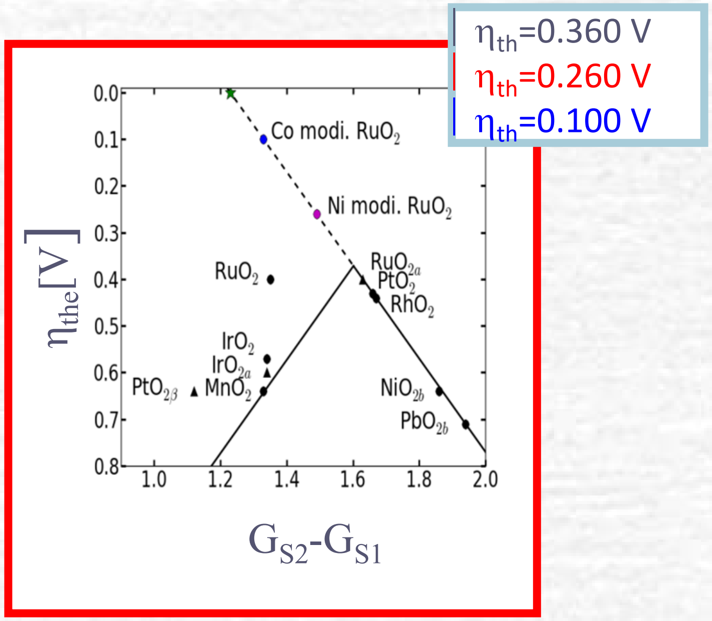
$U_{ORR}=\min(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e$

OER … e
surf…



Designing the viable catalyst

- maximising the activity
- maximising stability
- optimizing the feasibility



Minimizing the noble metal content

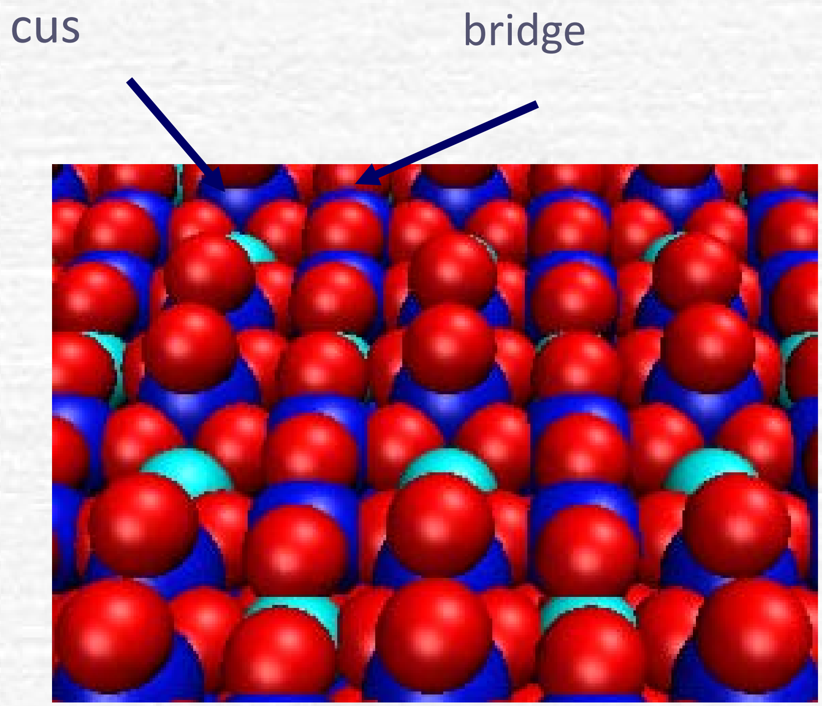
Optimizing the surface orientation (crystal morphology)

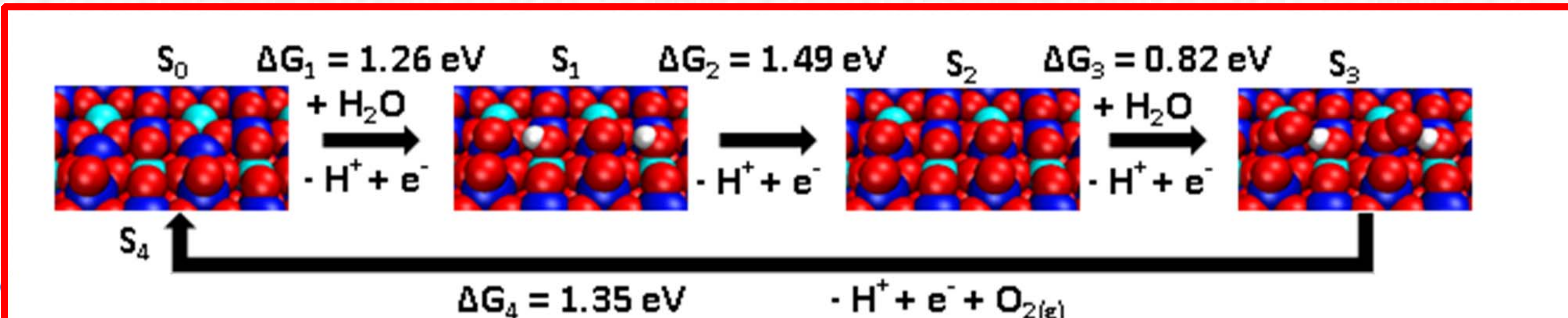
Maximising the No of active sites

Breaking volcano restrictions

OER activity control

Model of the [110] surface of $Ru_{1-x}Me_xO_{2-\delta}$





Substituted ruthenia

- translation symmetry unaffected

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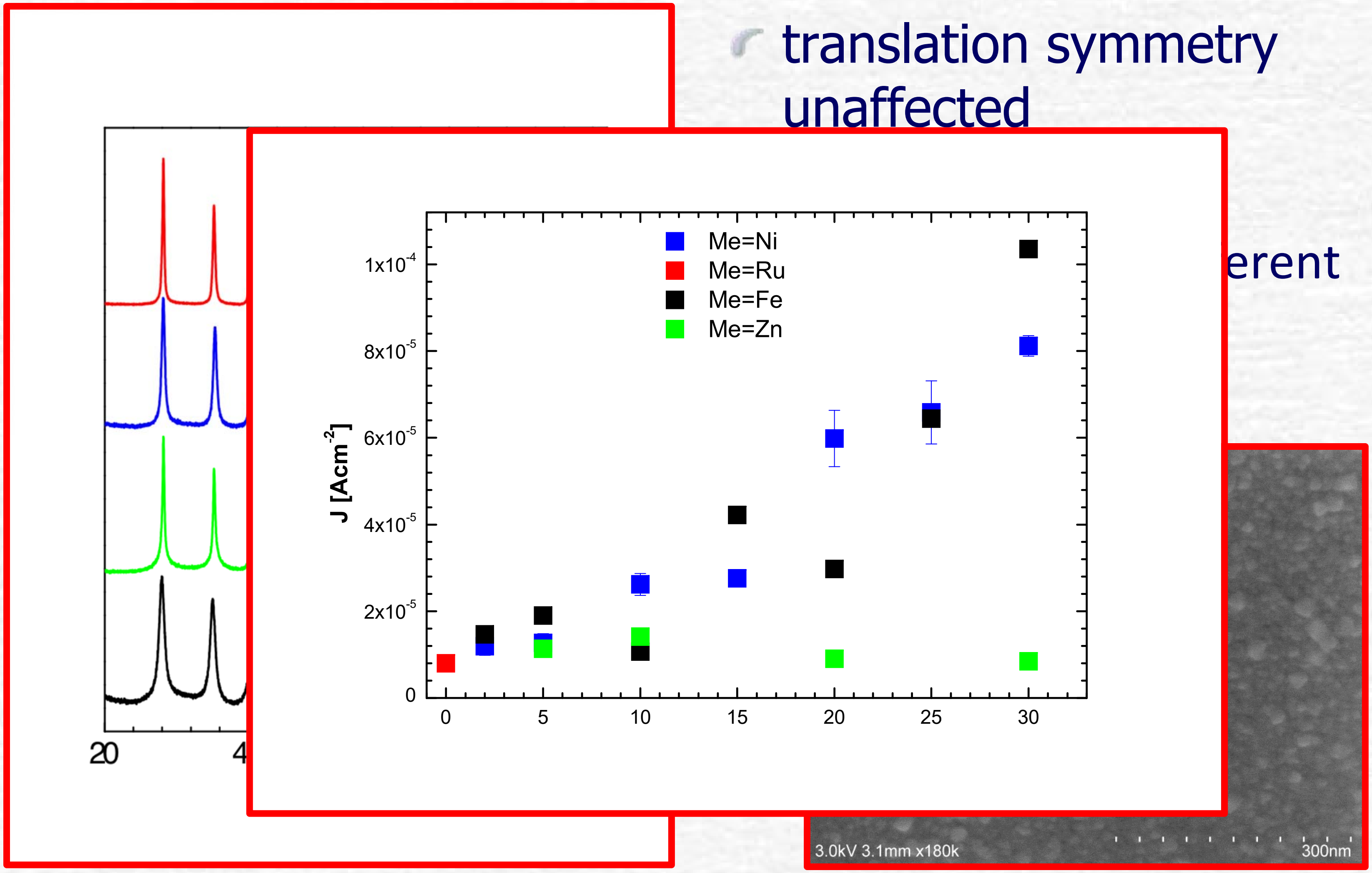
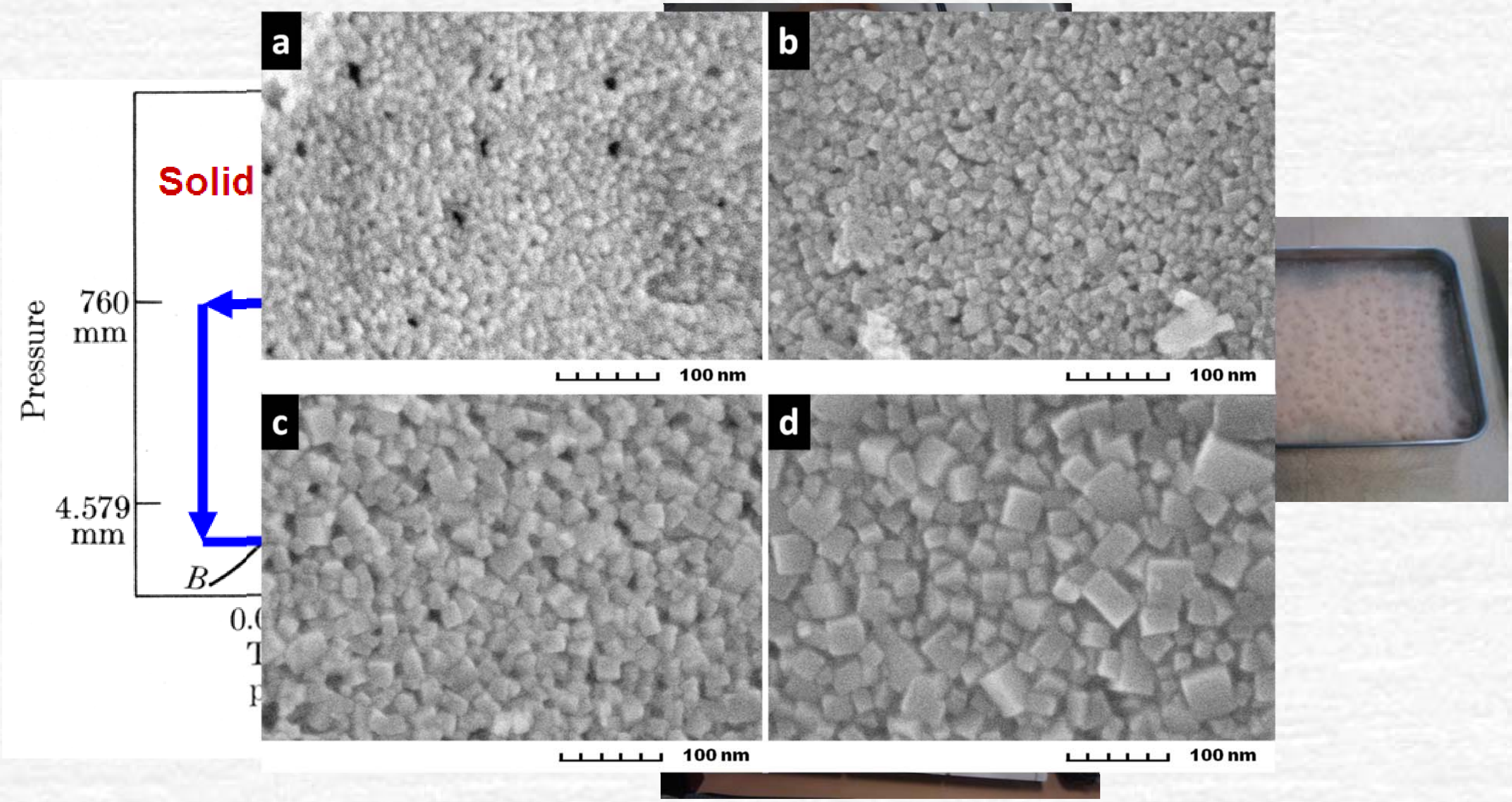
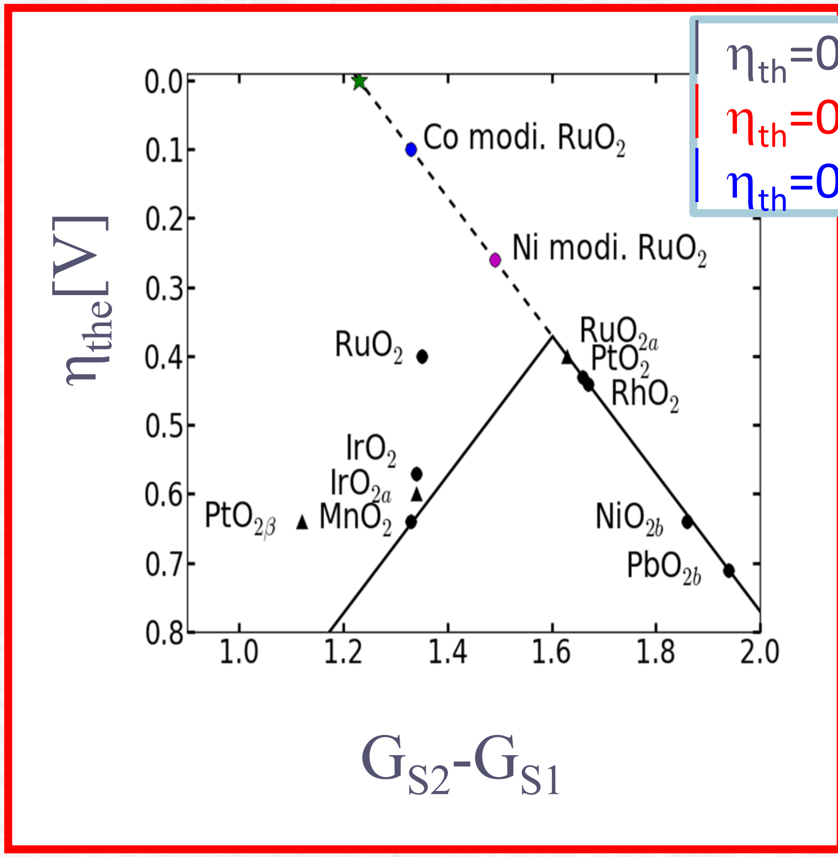


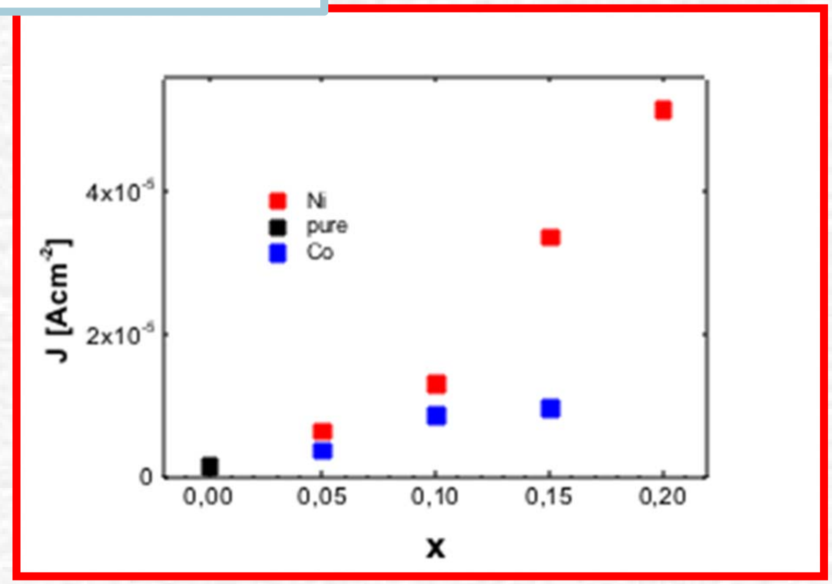
Spray-Freezing/Freeze-Drying Synthesis



Corrected OER volcano



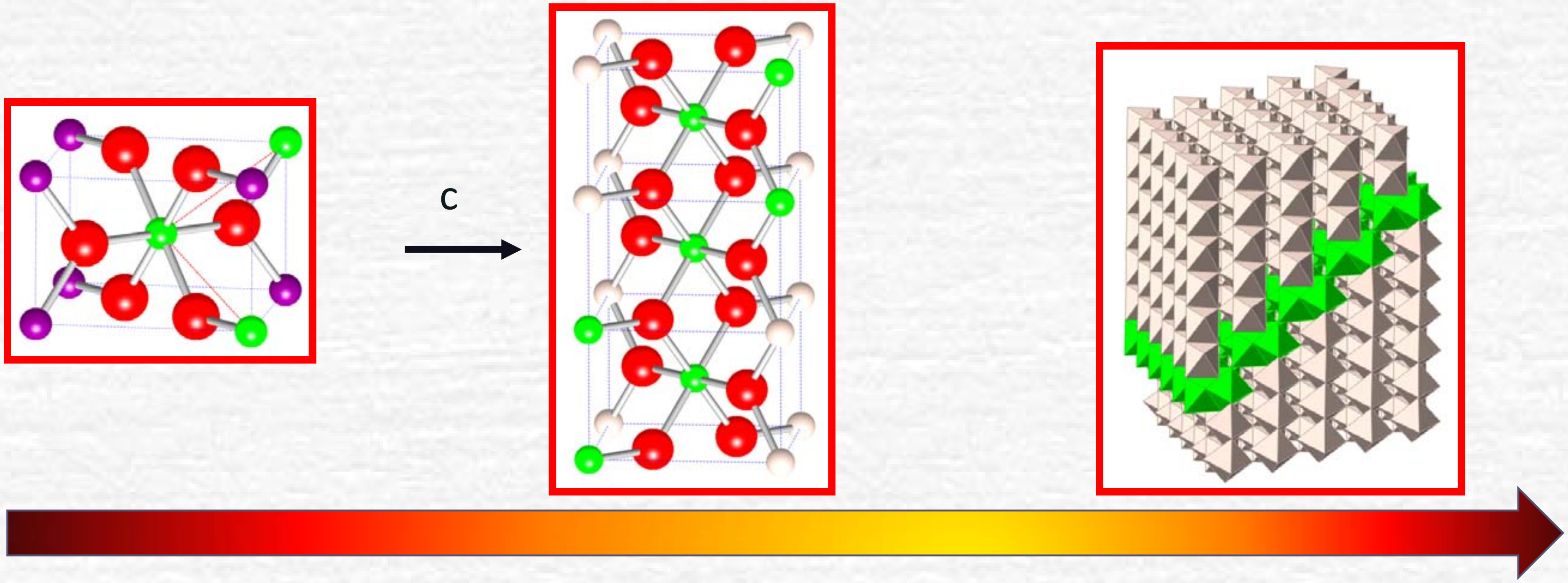
η_{th}=0.360 V
η_{th}=0.260 V
η_{th}=0.100 V



Bendtsen Halck et al, PCCP, 16, 13682 (2014).

Observed OER activity improvement does not match the theoretical prediction mainly for Co!

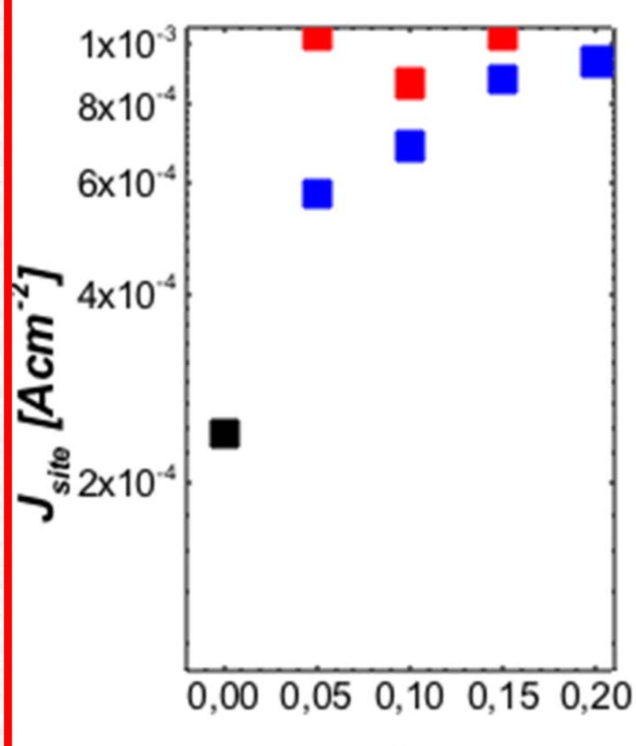
Me clustering



Dopant content

Concentration dependence of the cluster shape decreases in order Ni, Co.

OER – theory vs. experiment



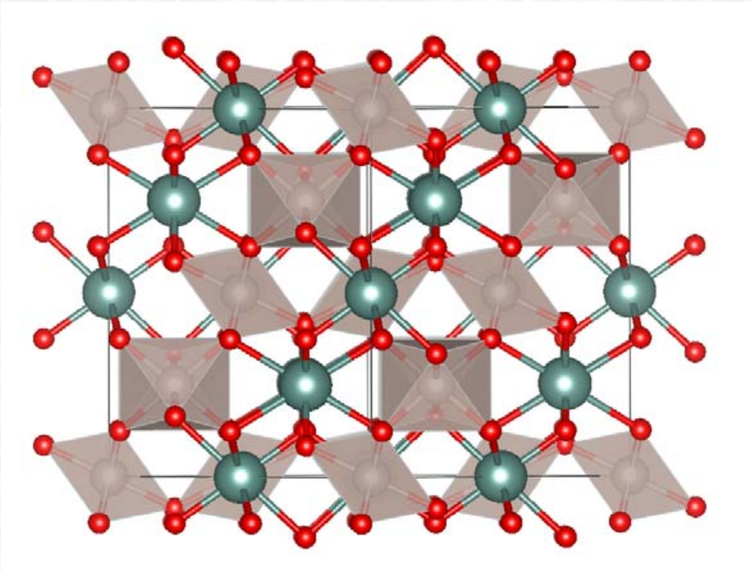
- Theoretical models are non-realistic
- Experimental activity summarizes contributions of doped as well as non-doped surface
- Correction for number of sites and cluster geometry

- **Activity can be solved**
- **Stability and feasibility remains an issue!**

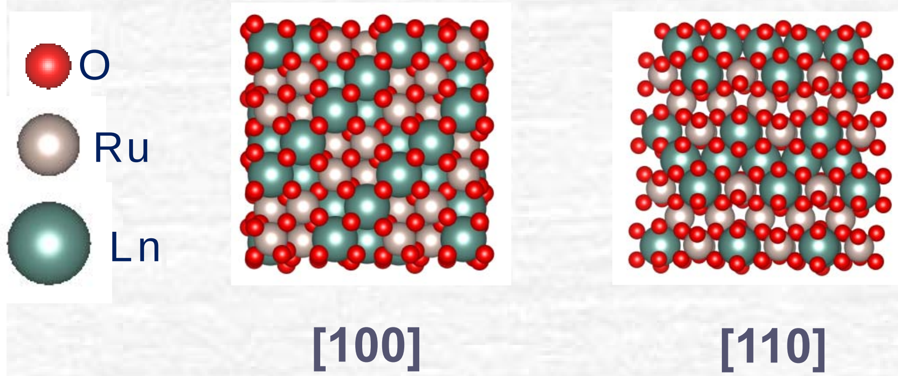
OER stability control

Ru/Ir oxide structures

- **Ru- and Ir- Pyrchlores ($A_2B_2O_7$) with different Lanthanides (Ln)**



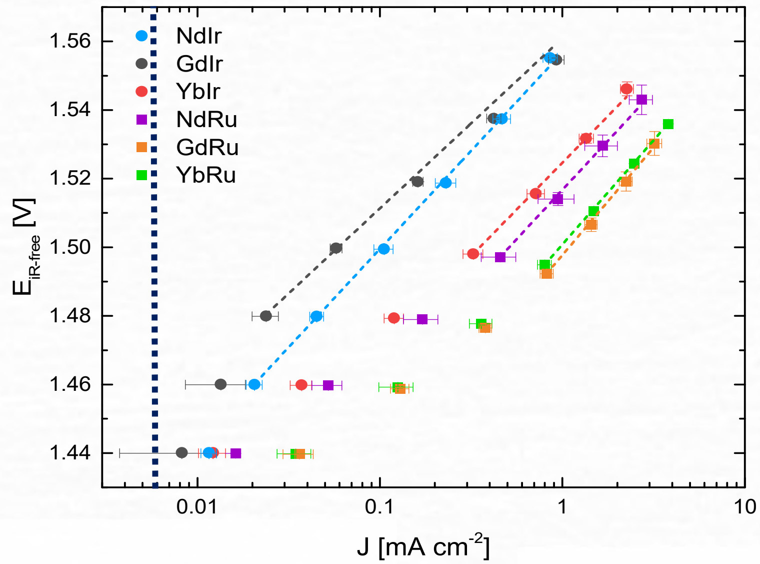
pyrochlore structure



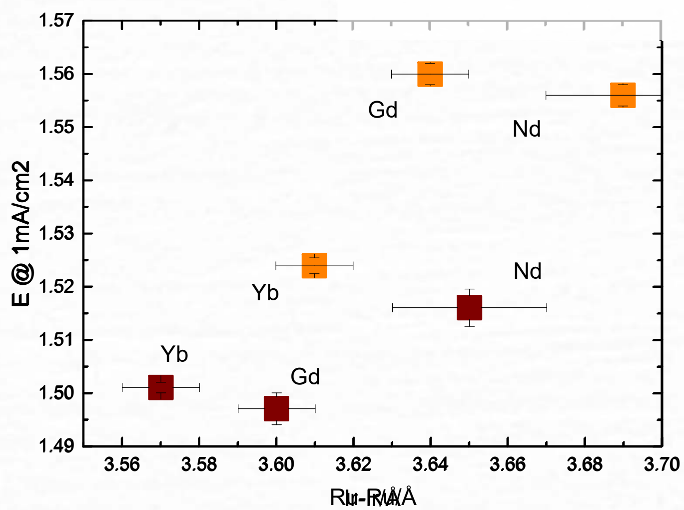
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- **Ln: range in ionic radii**
  - **expansion/contraction of lattice → electronic structure**
  - **The structure is cubic – i.e. the same local environment for all present metal cations**

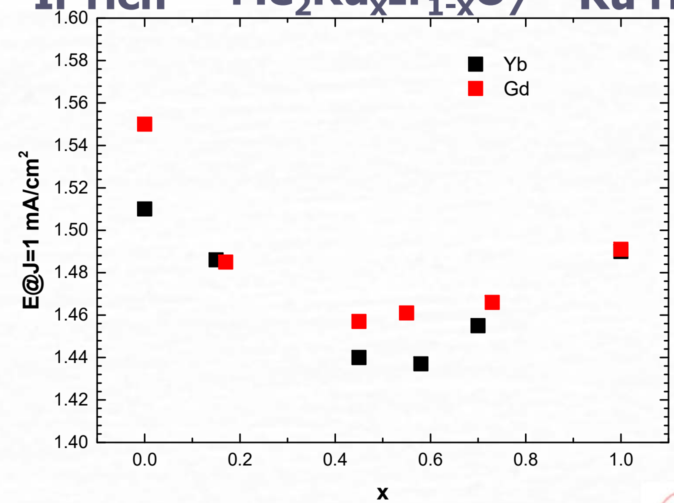
Pyrochlore - synergetic behavior



➢ **Activity related to Me-Me bond length**



Ir rich **$Me_2Ru_xIr_{1-x}O_7$** **Ru rich**



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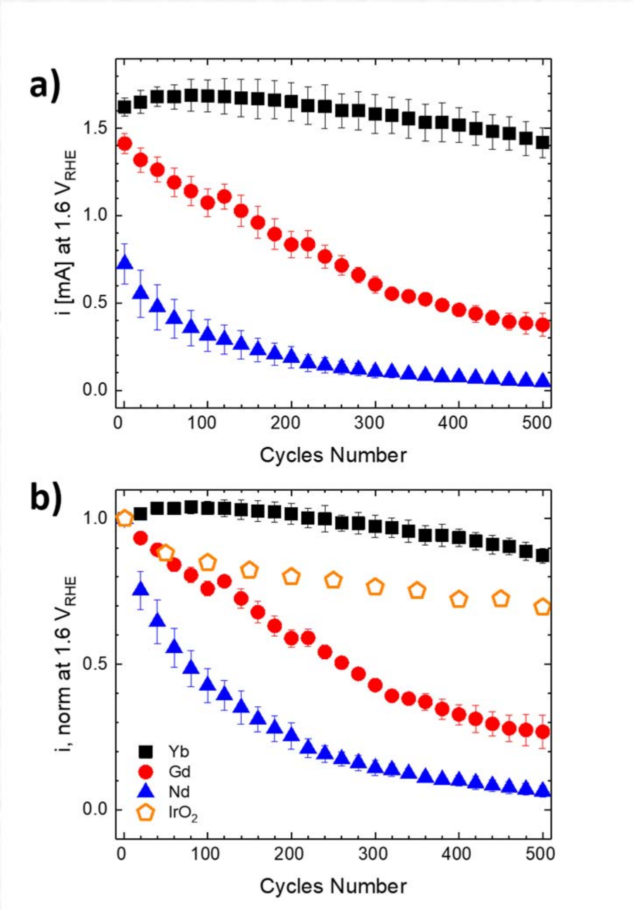
Pyrochlore stability



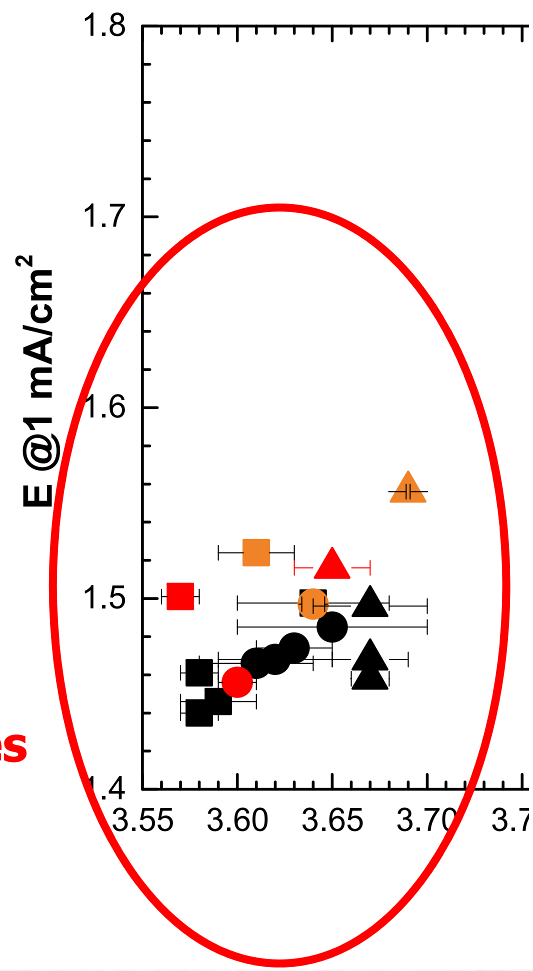
Stability is improved beyond the benchmark catalyst

Proper stabilization of the structure is needed to optimize the stability

Electrocatalytic energy storage

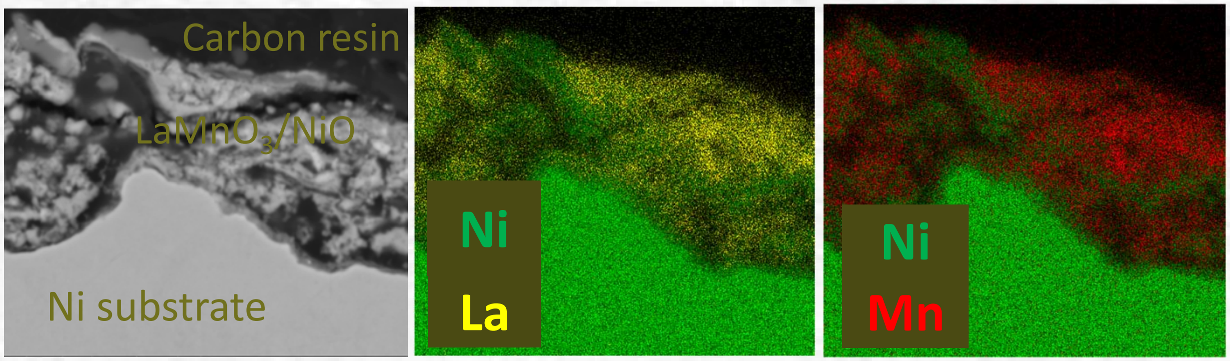
Way forward?

General applicability of the approach?

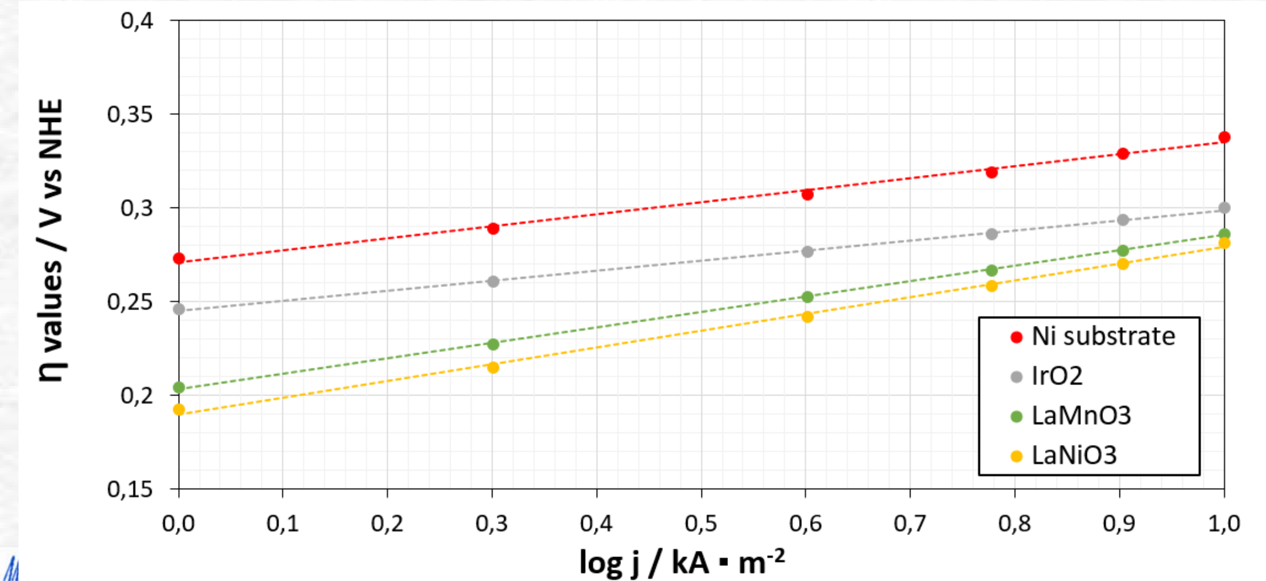


pyrochlores

Engineered electrode testing



Cross section (EDX Elemental Mapping) analysis of the coating confirmed the homogeneity of $LaMnO_3$ particles in NiO.



50 to 60 mV gain vs Ni substrate

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DE NORA

Innovative Training Network

- 7 partners 5 academic and 2 industrial
- Prague, Leiden, Copenhagen, Helsinki, Taragona, Milano and Amsterdam

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Conclusions

- **We can optimize the OER activity despite its complexity by local structure control**
- **If we understand and explore “descriptors” parameters of the process**
- **Nanoparticulate catalysts**
- **Complementarity of the approaches (different TRL levels) and competences need to be explored**
- **Large coordinated effort is needed**