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Molecular Engineering of Hybrid Layered Double Hydroxides for Energy Applications

chem2Dmat
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EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

Alvaro Seijas Da Silva

General introduction

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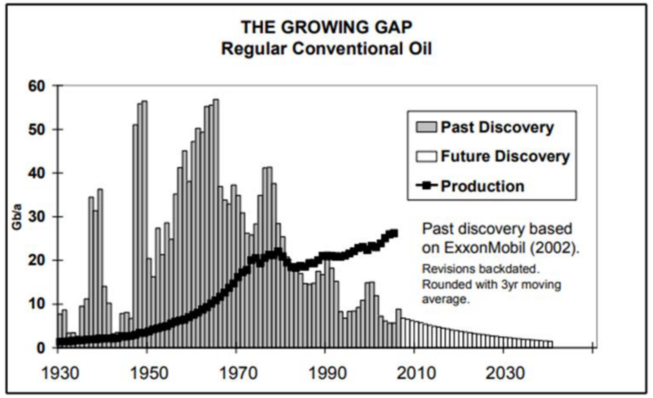
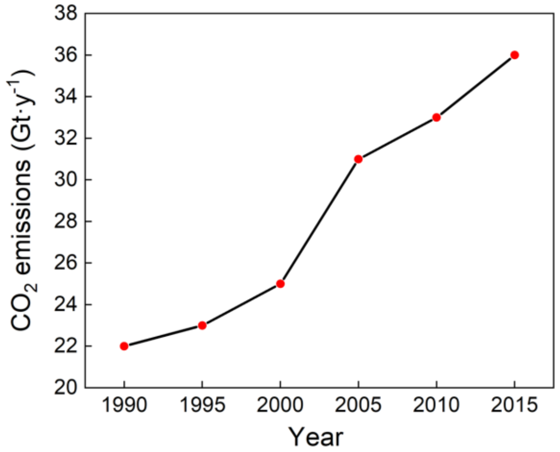
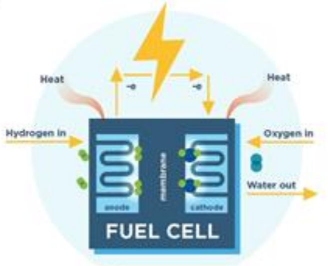
• Energy and environmental problems





• Highly efficient energy conversion and storage systems



To achieve this are mandatory

High performance electroactive materials

General introduction

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LDHs are potential electroactive materials.

- Good electrochemical behaviour
- Chemical versatility
- Electrochemical stability
- Low-cost

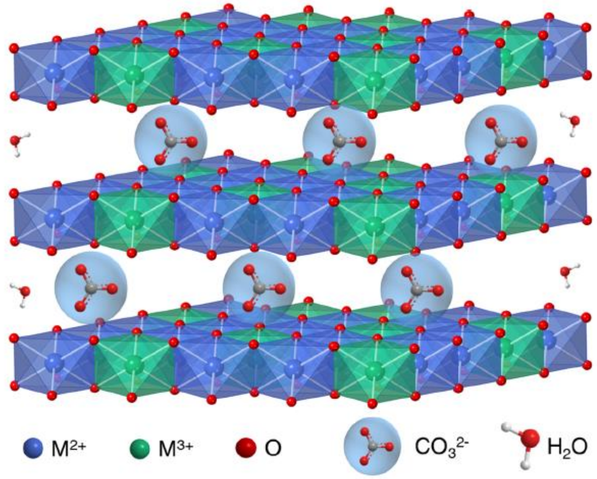
• Layered double hydroxide (LDH)

- ❑ LDH are laminar materials, composed of sheets of positive charge metal hydroxides and anions placed between the layers compensating the charges.

- ❑ Hydrotalcite-like structure of $[M^{II}_{1-\chi}M^{III}_{\chi}(OH)_2]^{\chi+}(A^{n-})_{\chi/n}\cdot mH_2O$, the range $0.2 \leq \chi \leq 0.33$.

- ❑ High tunability regarding the metallic composition, metallic ratio and the interlayer anion.

- ❑ Interesting application in supercapacitor and water splitting fields.



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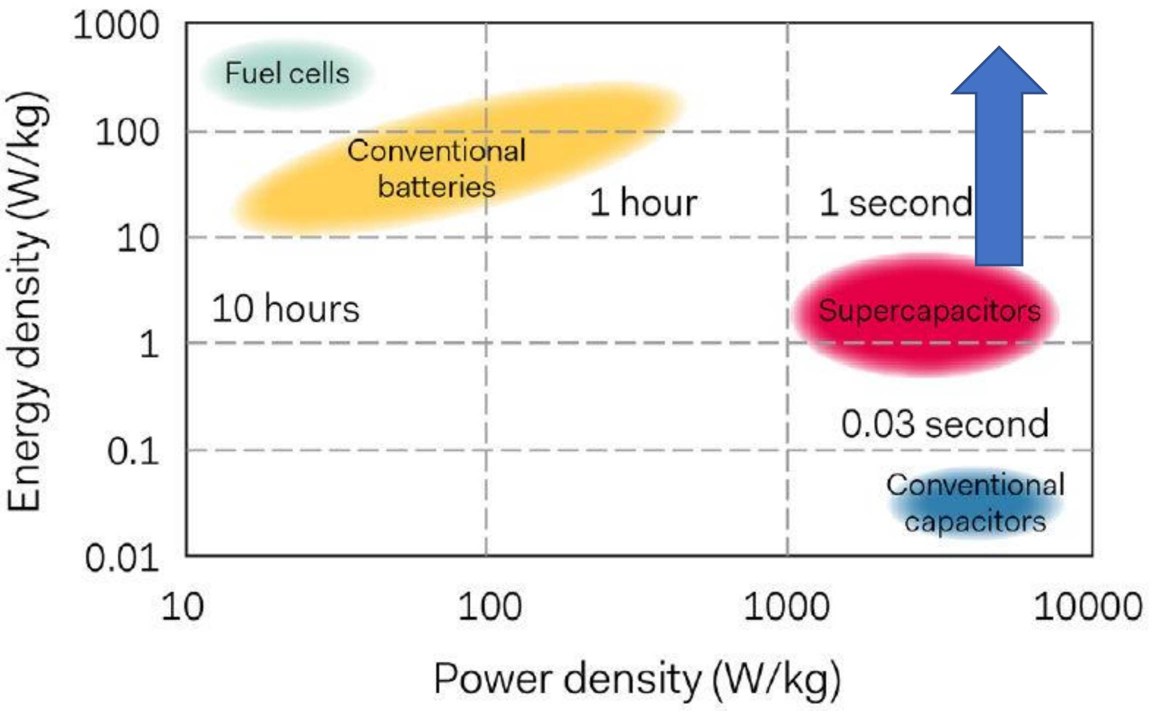
- **Layered double hydroxides in supercapacitors and water splitting technology**

Why introduce LDH in supercapacitor and in water splitting?

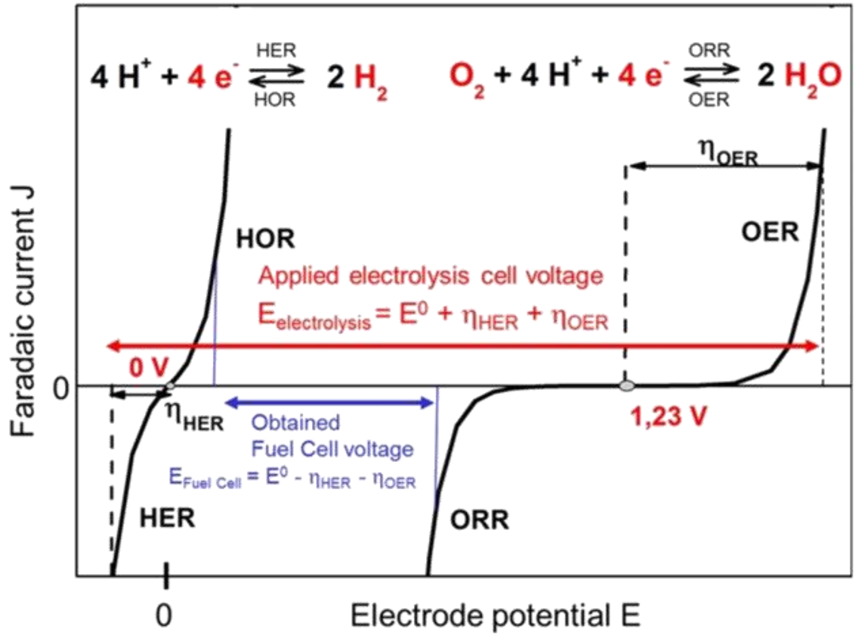
Supercapacitors



Increase the energy density of supercapacitor

Water splitting

Oxygen evolution reaction (OER) is the reaction with the greatest kinetic barrier



Obtain efficient catalysts for OER, based on abundant metals

General introduction

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• Layered double hydroxides in supercapacitors and water splitting technology

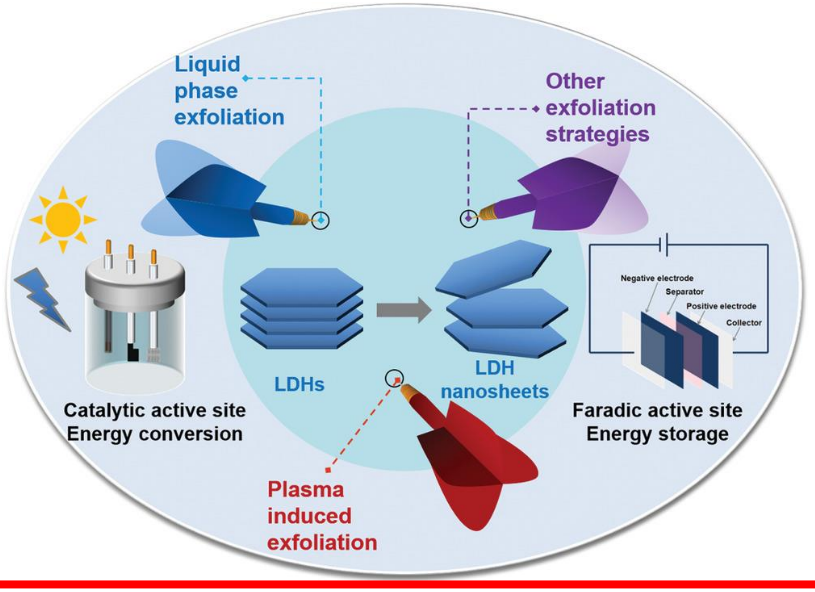
As is known for other 2D materials, the exfoliation of LDH allows to improve their electrochemical activity.

REVIEW

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Advanced Exfoliation Strategies for Layered Double Hydroxides and Applications in Energy Conversion and Storage

*Chen Chen, Li Tao, Shiqian Du, Wei Chen, Yanyong Wang, Yuqin Zou, and Shuangyin Wang**



Inconveniences

- The current exfoliation strategies for LDHs are mostly in small amounts.
- Liquid phase exfoliation always needs excess solvents to delaminate and stabilize the LDH nanosheets.
- The LDH nanosheets obtained usually have a wide range of thicknesses and lateral sizes even after separation.

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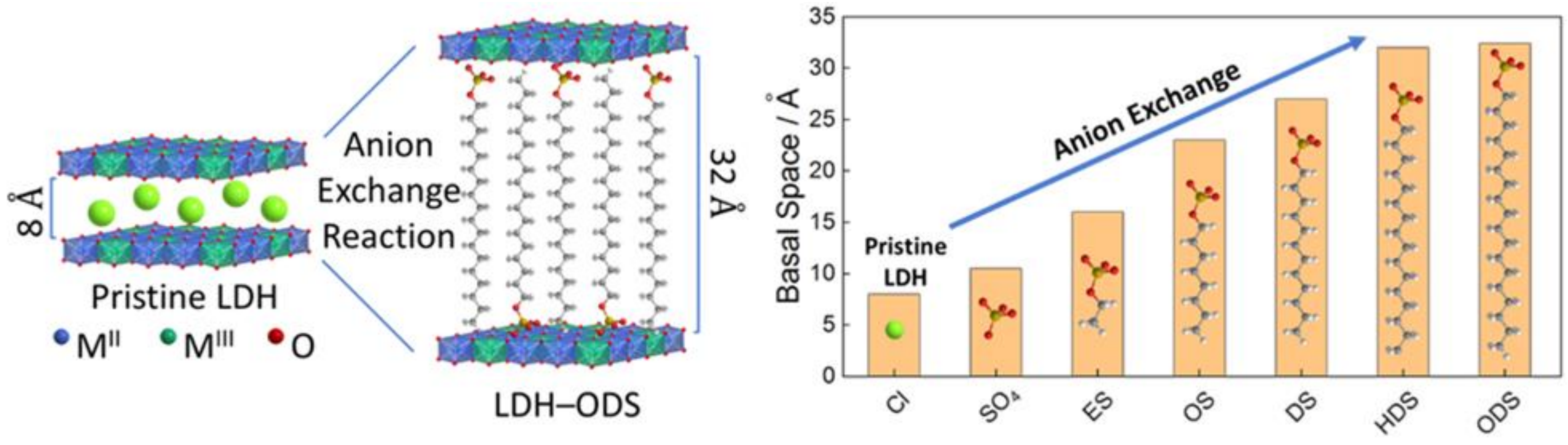
- **Layered double hydroxides for supercapacitors and catalysts for the OER**

Molecular spacing as an alternative to exfoliation.



CoAl-LDH as electrode materials for supercapacitor

NiFe-LDH as electrocatalysts for the OER

Experimental section

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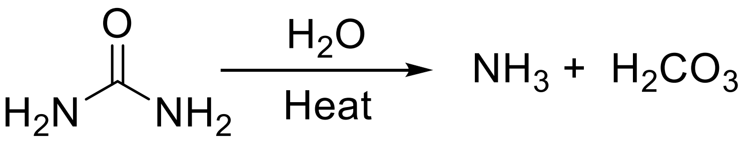
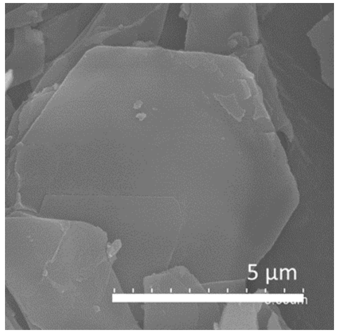
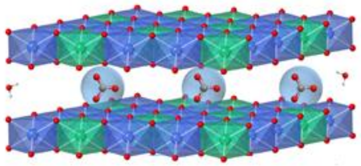
CoAl–LDH as electrode materials for supercapacitor

Homogeneous precipitation with urea → CoAl(2:1)-CO_3



urea

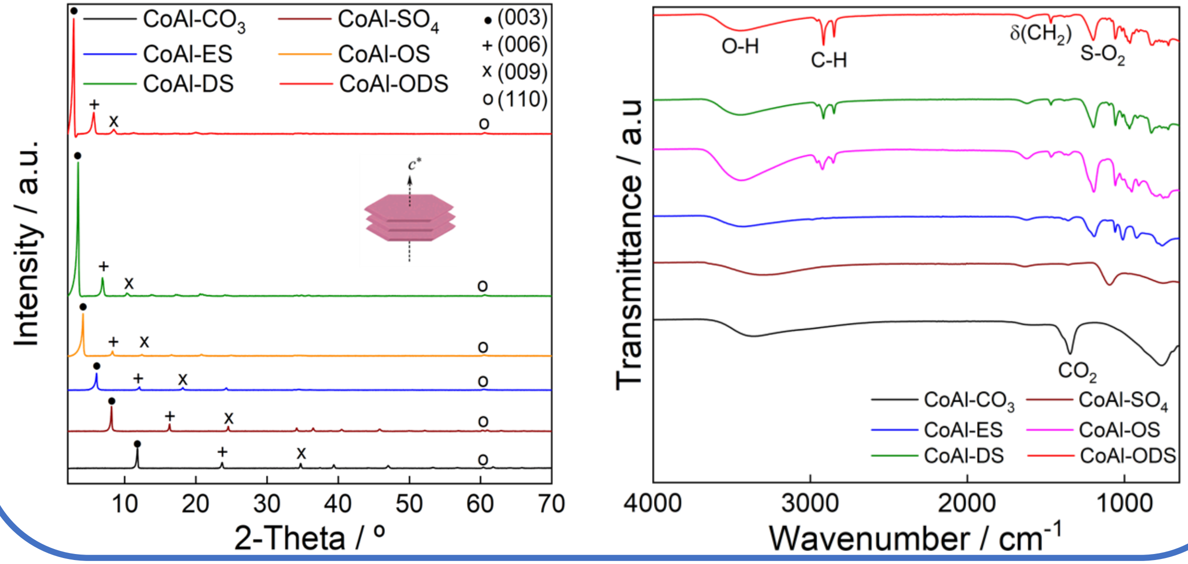




CoAl-CO_3

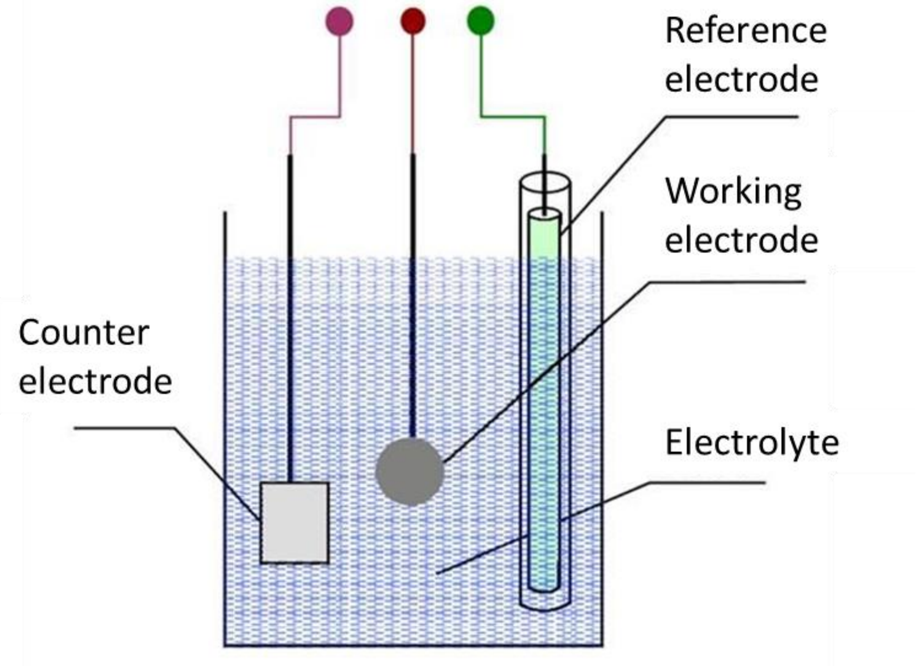
HNO_3 / $NaNO_3$ → CoAl-NO_3 → Ethanol:water Media / Surfactant

CoAl-surfactant family

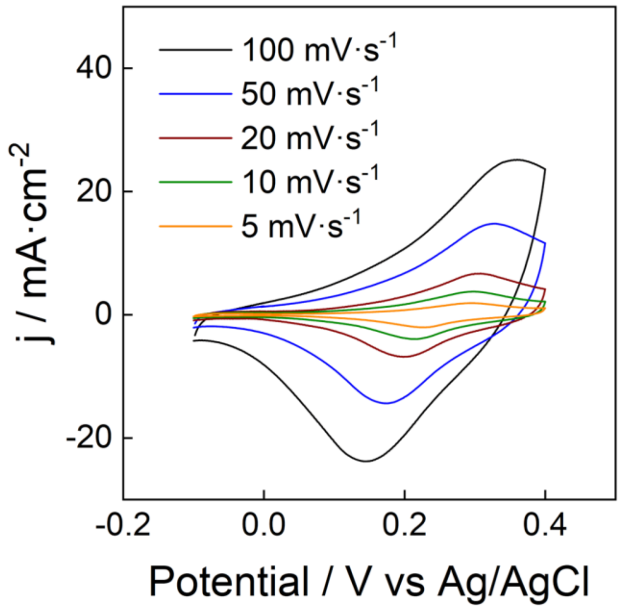


CoAl–LDH as electrode materials for supercapacitor

Electrochemical characterization



Working electrode: CoAl–LDH/Ni-Foam.
Counter electrode: stainless steel.
Reference electrode: Ag/AgCl.
Electrolyte: KOH 6 M.

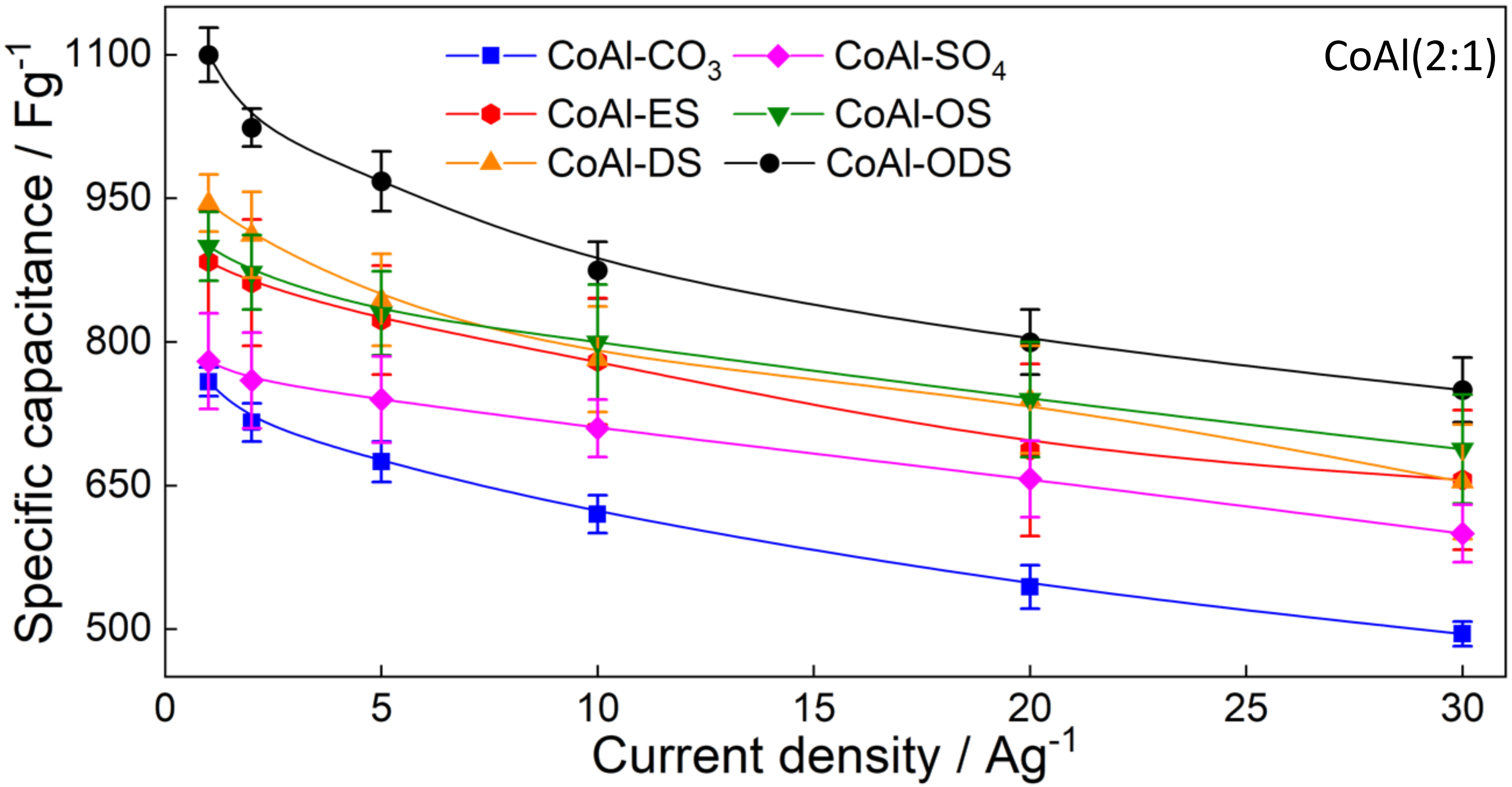


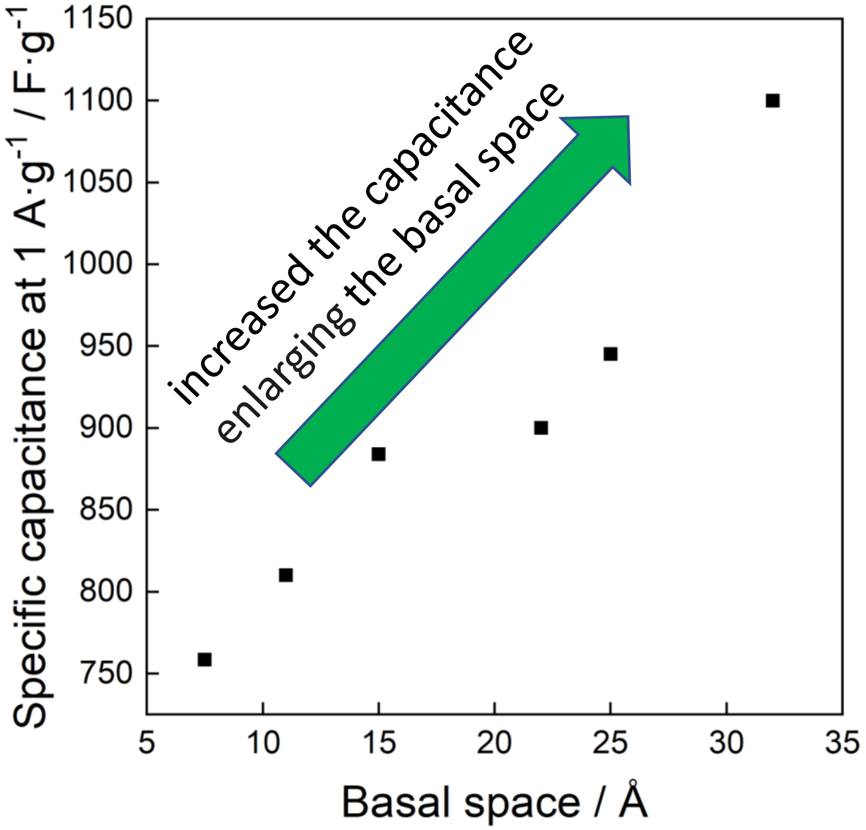
$$Co(OH)_2 + OH^- \leftrightharpoons CoOOH + H_2O + e^-$$

The specific capacitance was determined for all CoAl–LDH family:

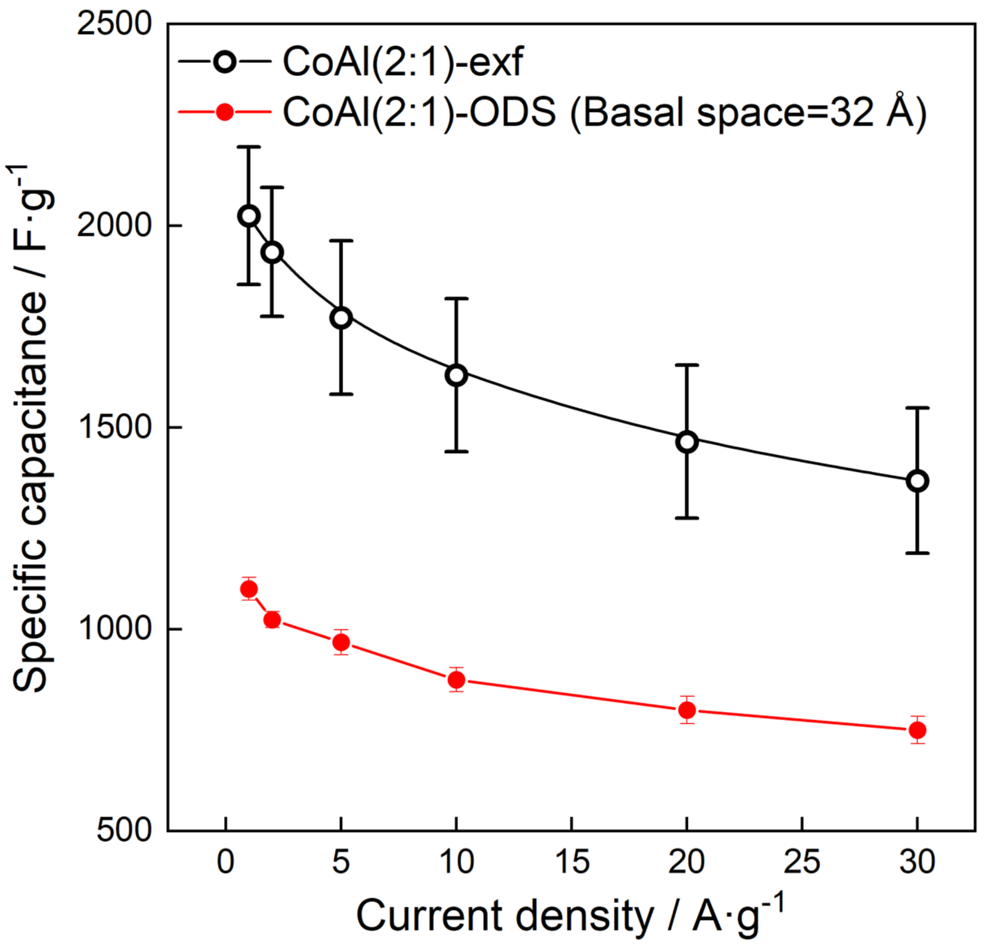
$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

CoAl–LDH as electrode materials for supercapacitor





CoAl–LDH as electrode materials for supercapacitor



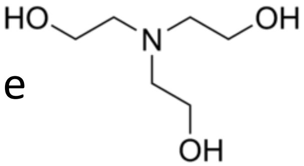
CoAl-ODS advantage

- Scalable production.
- Possibility of isolate the material as solid.
- All the material has the same characteristics.
- An electrochemical behaviour more homogeneous.

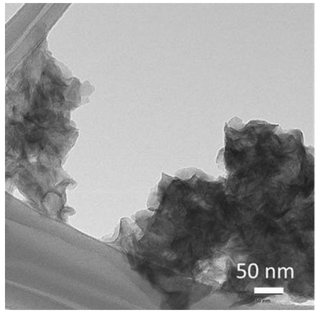
NiFe–LDH as electrocatalysts for the OER

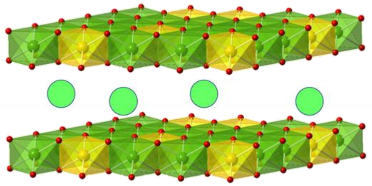
Hydrothermal synthesis with TEA in excess → NiFe(3:1)-Cl

Triethanolamine



pKa= 7.8





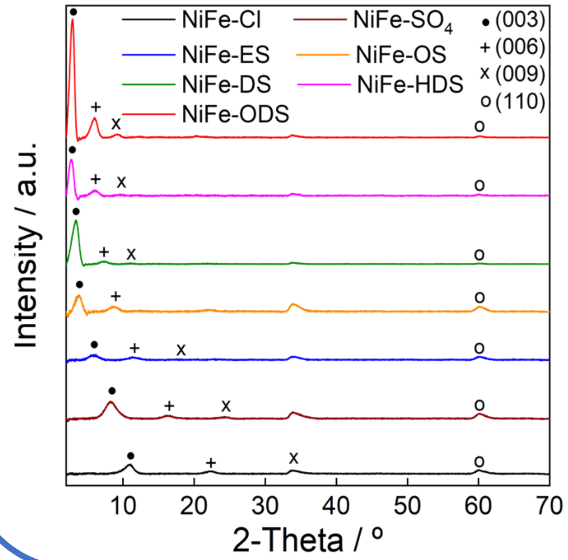
NiFe-Cl

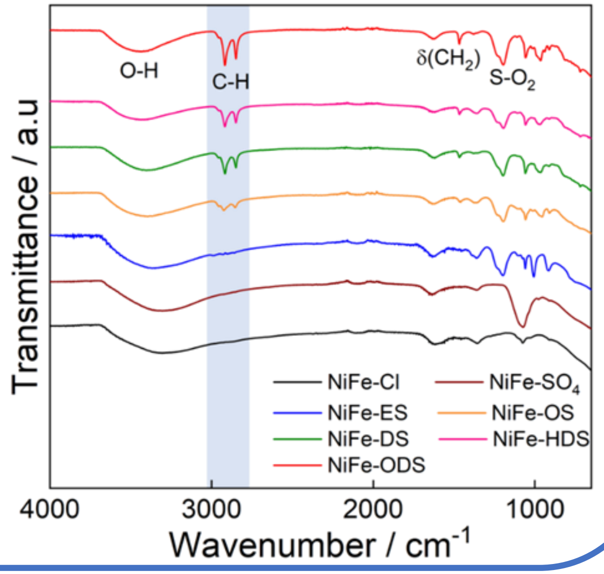
Surfactant

Ethanol:water media

One step surfactant exchanges

NiFe-surfactant family





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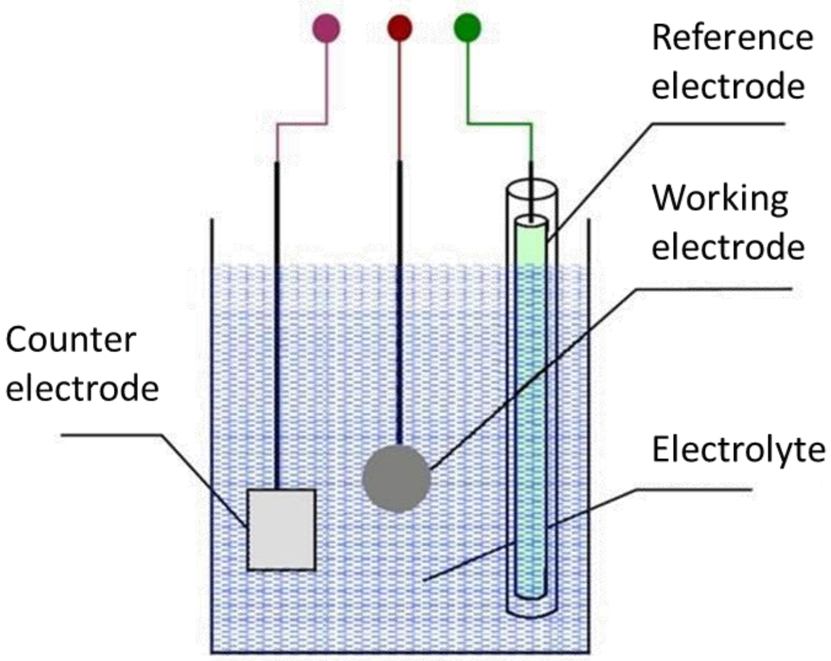
NiFe–LDH as electrocatalysts for the OER

Electrochemical characterization



Working electrode: NiFe–LDH/Ni-Foam.
Counter electrode: stainless steel.
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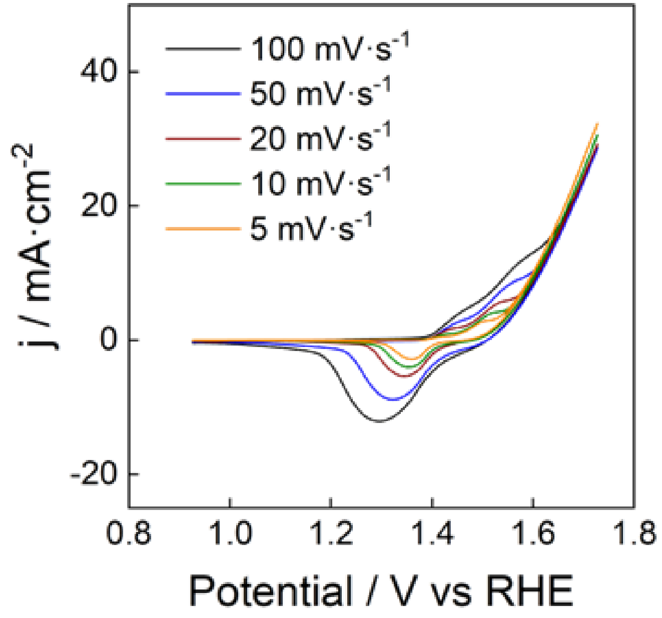
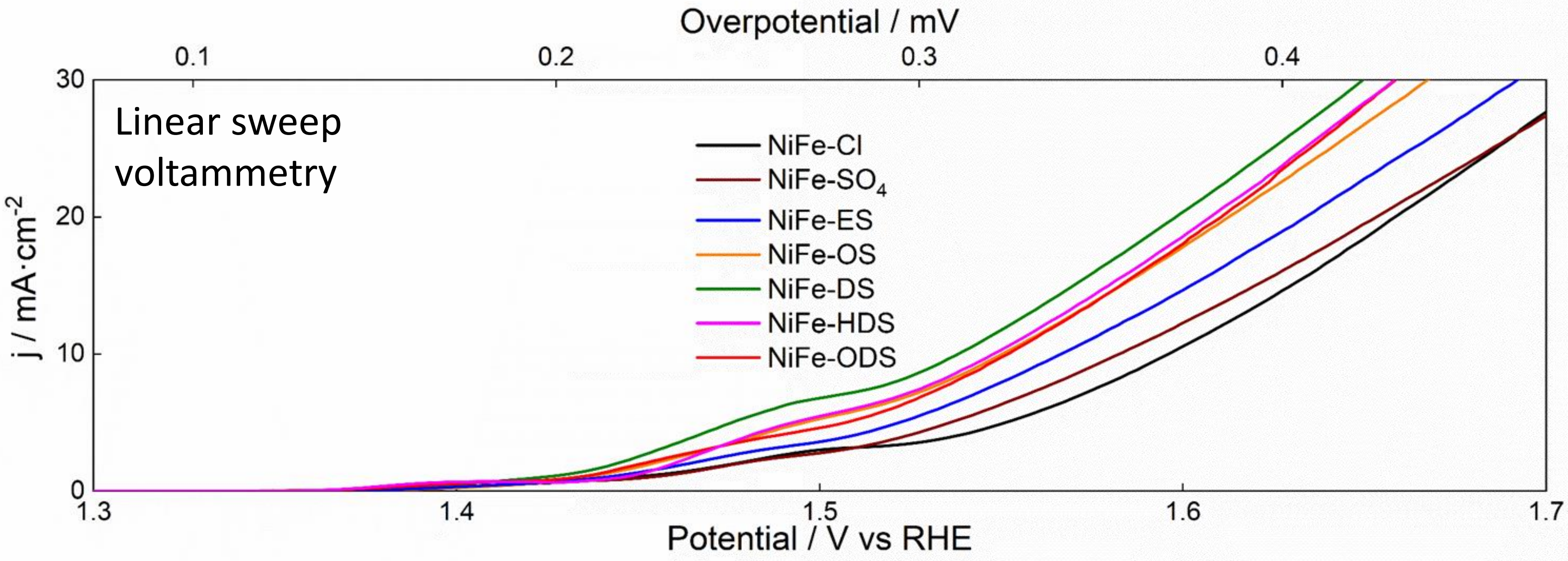


$$Ni_3Fe(OOH)_3 + 3\,H_2O\ +\ 3\,e^- \leftrightarrows Ni_3Fe\,(OH)_6 + 3\,OH^-$$

- ❑ **Oxygen evolution reaction (OER) at 1 M KOH**

$$4\,OH^- \leftrightarrows 2\,H_2O + O_2 + 4\,e^-$$

NiFe–LDH as electrocatalysts for the OER



To compare the efficiency of the surfactant-intercalated NiFe family as electrocatalysts for the OER, three parameters were studied:

Tafel slope

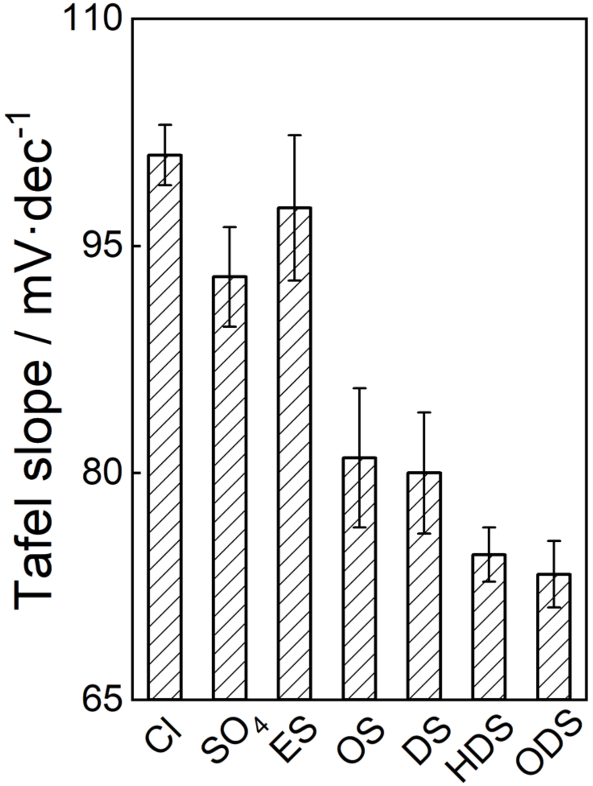
$$\eta = \mathrm{A} \cdot \log\left(\frac{i}{i_0}\right)$$

Overpotential at 10 mA·cm^{-2}

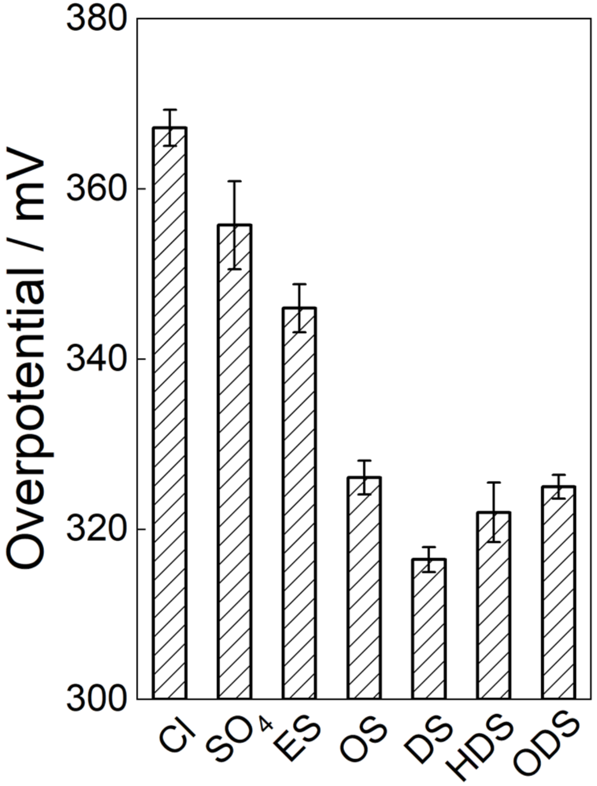
Stability

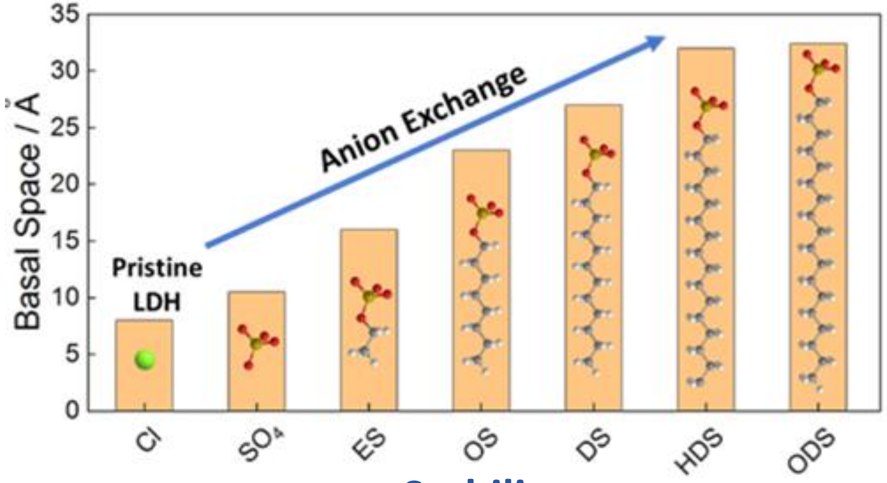
NiFe–LDH as electrocatalysts for the OER

Tafel slope

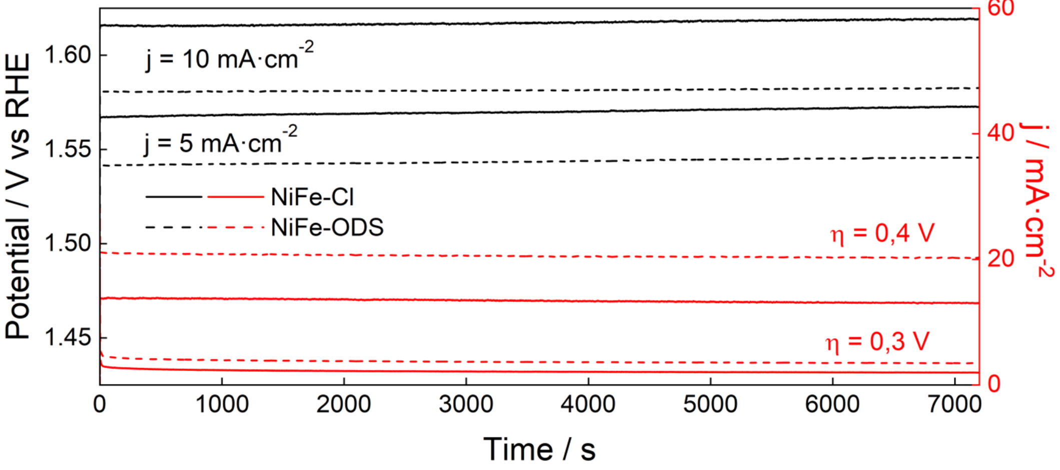


Overpotential at 10 mA·cm^{-2}





Stability



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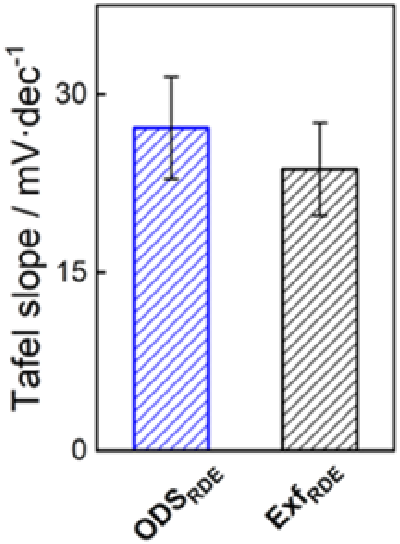
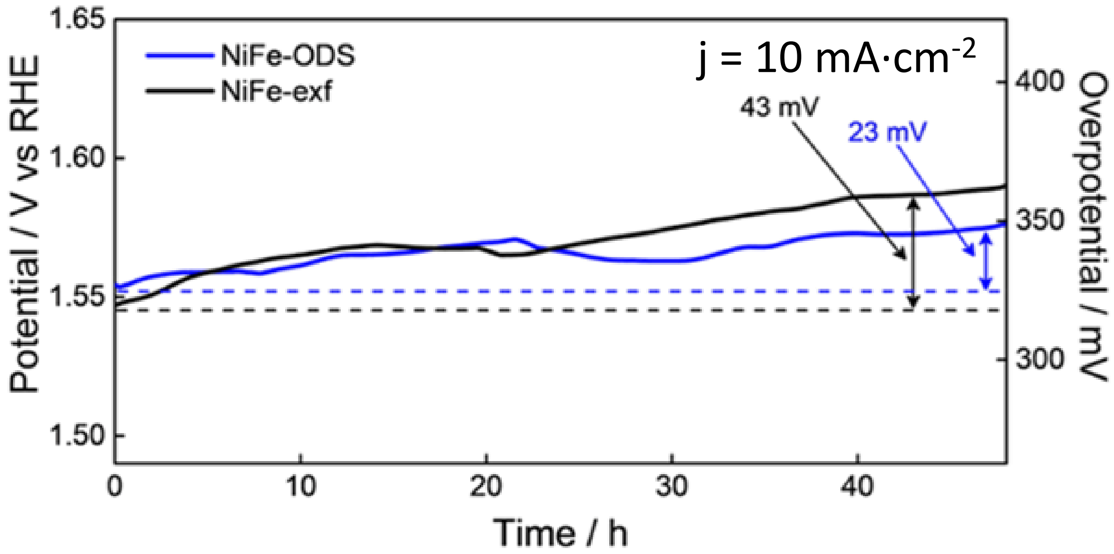
NiFe–LDH as electrocatalysts for the OER

NiFe-ODS is compare with an exfoliated NiFe-LDH





NiFe -ODS advantage

- Scalable production.
- Possibility of isolate the material as solid.
- All the material has the same characteristics.
- Very similar catalytic performance and better long-time stability.

Take-home message

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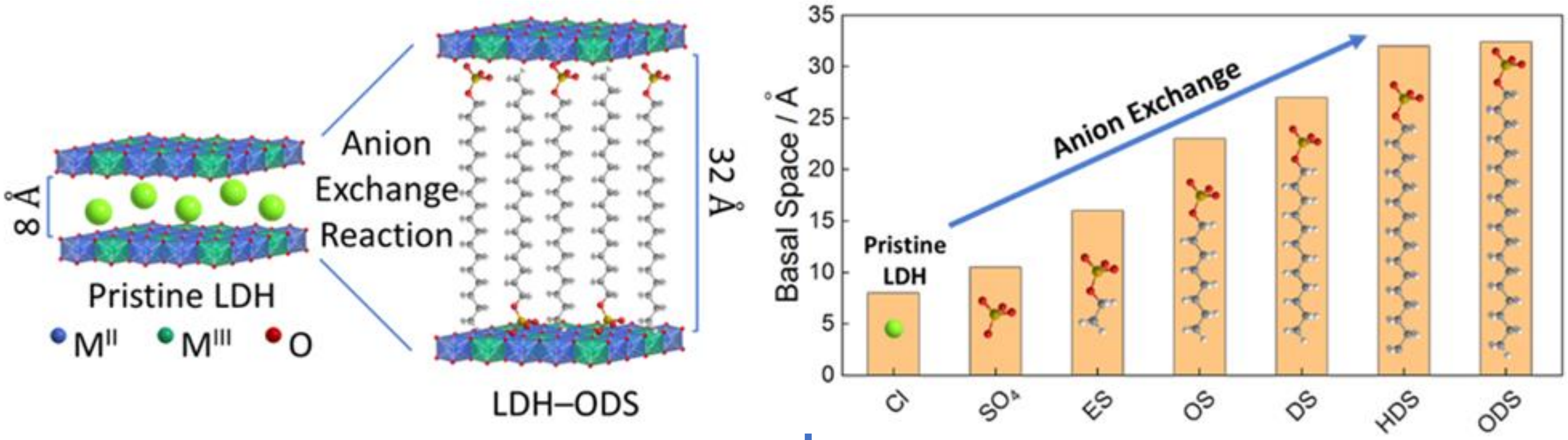
The molecular spacing of LDH



allows to obtain better performance

CoAl-LDH as electrode materials for supercapacitor

NiFe-LDH as electrocatalysts for the OER

even better than the LDH obtained by liquid exfoliation

All RTMM members (UV/ICMol)
Prof. Eugenio Coronado

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Thanks for your attention!