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Investigation on Layered Double Hydroxides as potential electrocatalysts for CO_2 reduction reaction to CO: in-situ IR spectroscopy studies

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INTRODUCTION

INTRODUCTION

The **electrochemical CO_2 reduction reaction** (**CO2RR**) to CO is a promising strategy for the CO_2 conversion [1-3].

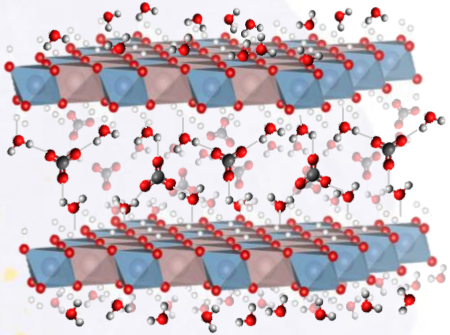


Figure 1. Example of LDH structure.

Among the possible materials can be used for CO2RR, the **Layered Doubled Hydroxides** (**LDHs**) are good candidate since they have[4]:

- Strong affinity with CO_2 in water.
- High stability in basic electrolytes.
- High ion conductivity.
- High affordability of the components.

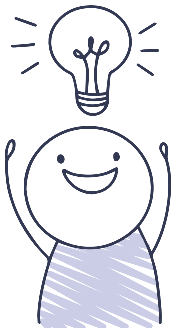
[1]X. Duan et al., *Adv. Mater.*, 29 (**2017**) 1701784.
[2]R. Nakazato et al. *RSC Sustain.* (**2023**), submitted.
[3]N. Yamaguchi at al. *J. Asian Ceram. Soc.* (**2023**), submitted.
[4]Y. Furukawa et al. *Solid State Ionics.*, 192 (**2011**) 185–187.

INTRODUCTION

This work is part of the H2020 European Founding project “**4AirCRAFT**” Air Carbon Recycling for Aviation Fuel Technology (GA ID 101022633).

Other researchers from the project joint the ICCDU23 with oral contribution, **Dr. Elias Rodriguez Jara** and **Dr. Vanesa Gil**, who already introduced the aim of 4AirCRAFT.

For further information, visit our project’s website:
https://4aircraft-project.eu/



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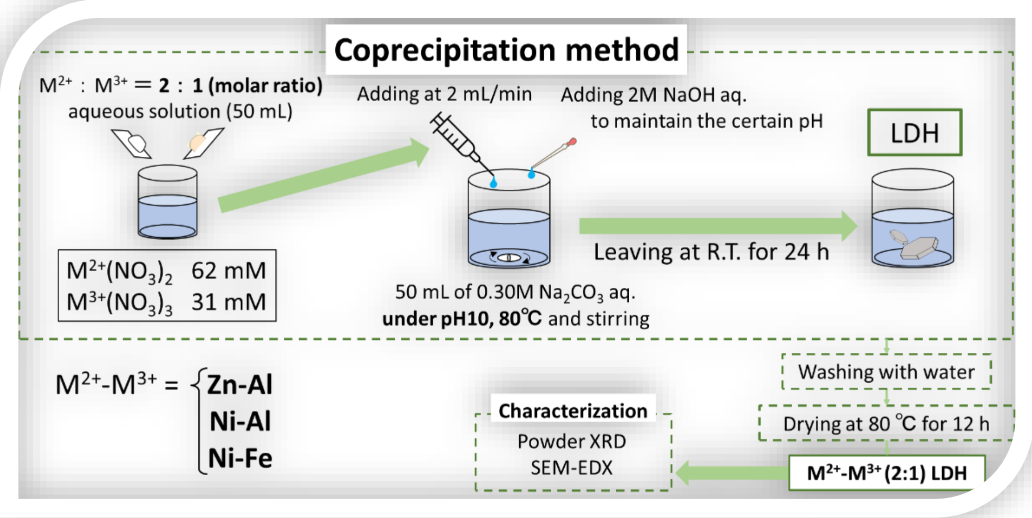
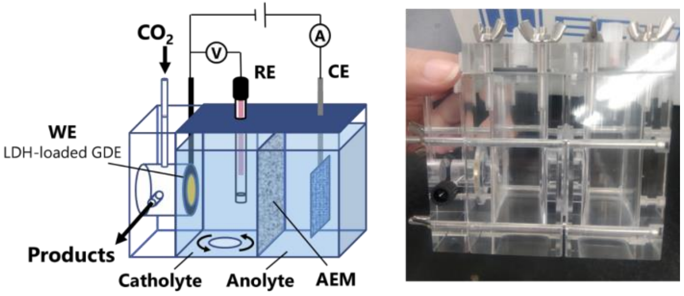
MATERIALS AND METHODS

MATERIALS AND METHODS

- The **synthesis** were performed by Hokkaido University, according to the scheme reported.





- **Electrocatalytic tests** were performed by a custom-made three-electrode setup

MATERIALS AND METHODS

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- **Thin deposition** on **ATR crystal**.
- Saturation of H_2O with N_2 (for 30 min).
- Then, saturation of H_2O with CO_2 (other 30 min).
- Spectra of materials at room temperature (RT).

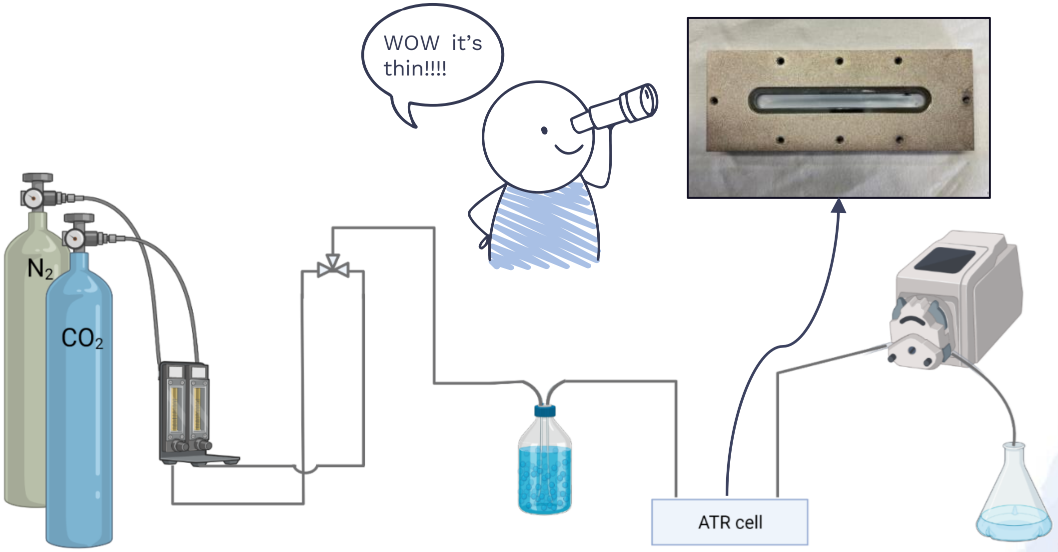
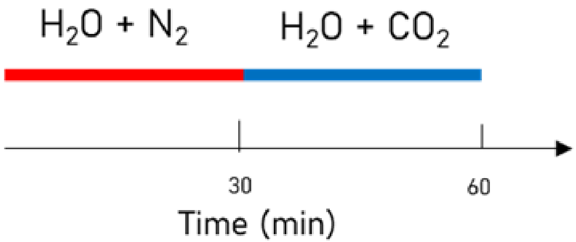


Figure 3. Set-up used for the FT-IR analysis.



Scheme of the experiment performed

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RESULTS

RESULTS

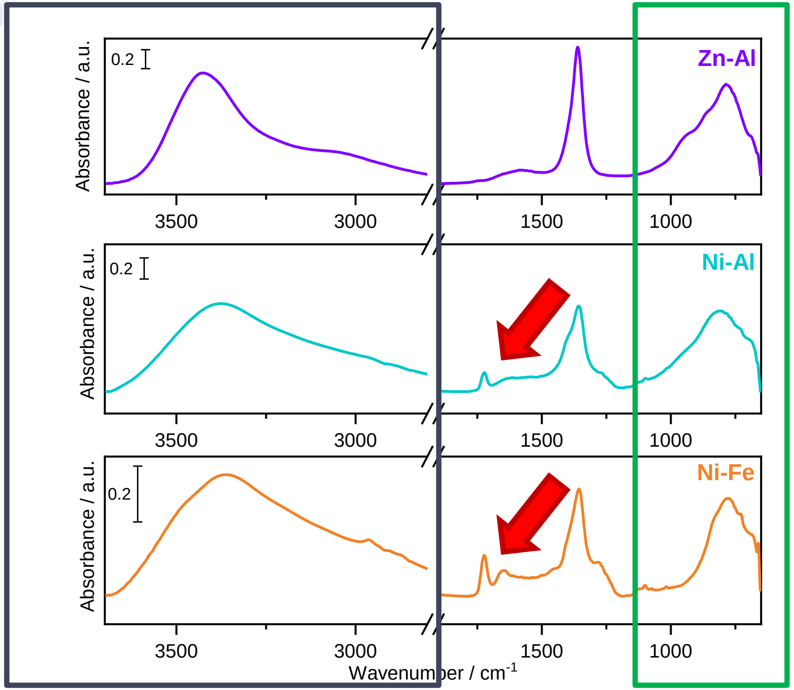
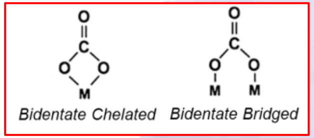


Figure 4. ATR-IR spectra in the 3700-650 cm^{-1} spectral region of dry Zn-Al LDH, Ni-Al LDH and Ni-Fe LDH.

- The samples exhibit a common **broad band** in the **high frequency region** (3500-2950 cm^{-1}).
- In the **low frequency region**, the samples have a broad band (1000-650 cm^{-1}) which derives from the superimposition of the ν2 of interlayer carbonate anions and the lattice HO-M-OH and M-OH vibrational modes.
- The **Ni-Al** and **Ni-Fe** LDHs interestingly show some additional peaks.



RESULTS

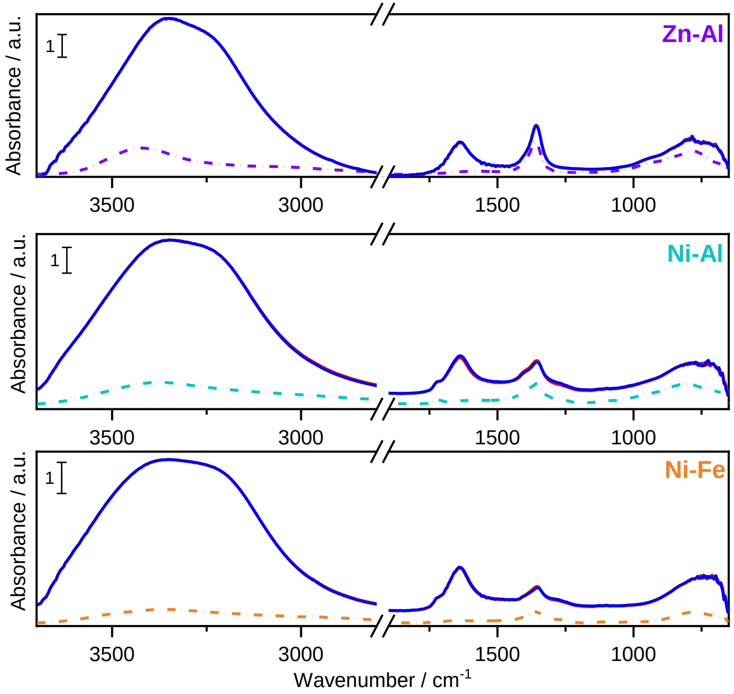
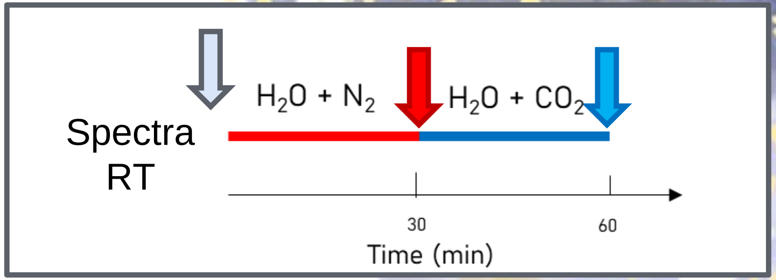
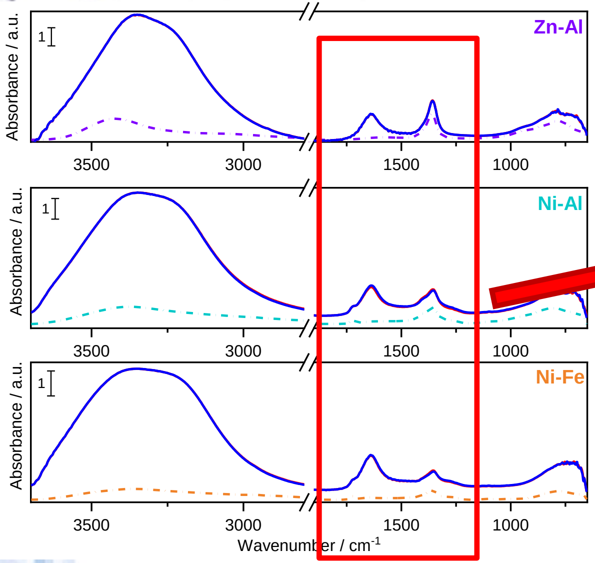


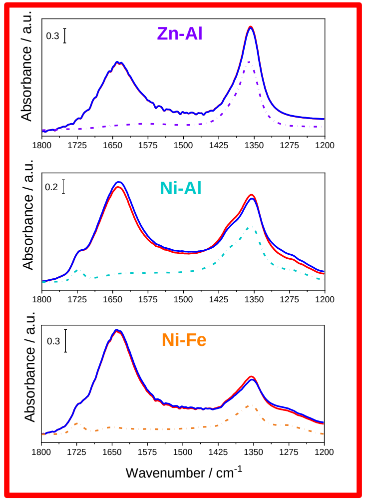
Figure 5. *In situ* ATR-IR spectra in the 3600-650 cm^{-1} spectral region of samples

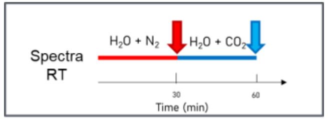


- The contact with H_2O caused an increase in the high frequency region bands associated to the **OH stretching**.
- The interaction of **CO_2** was responsible for the appearance of **surface (non-structural) carbonates-like species**.

RESULTS







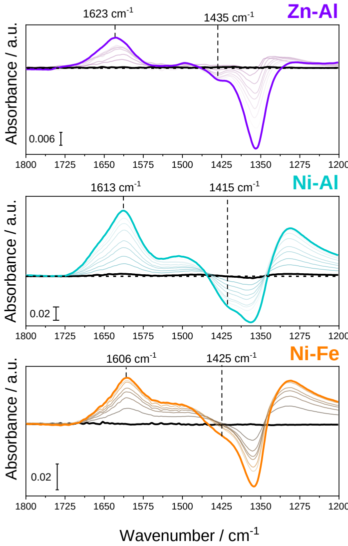


Figure 6. In situ ATR-IR spectra in the carbonate-like region (1800-1200 cm^{-1}) of: Zn-Al LDH, Ni-Al LDH and Ni-Fe LDH. The corresponding differential spectra (obtained by subtracting the spectra of the wet N_2-saturated sample to that of the wet CO_2-saturated sample).

RESULTS

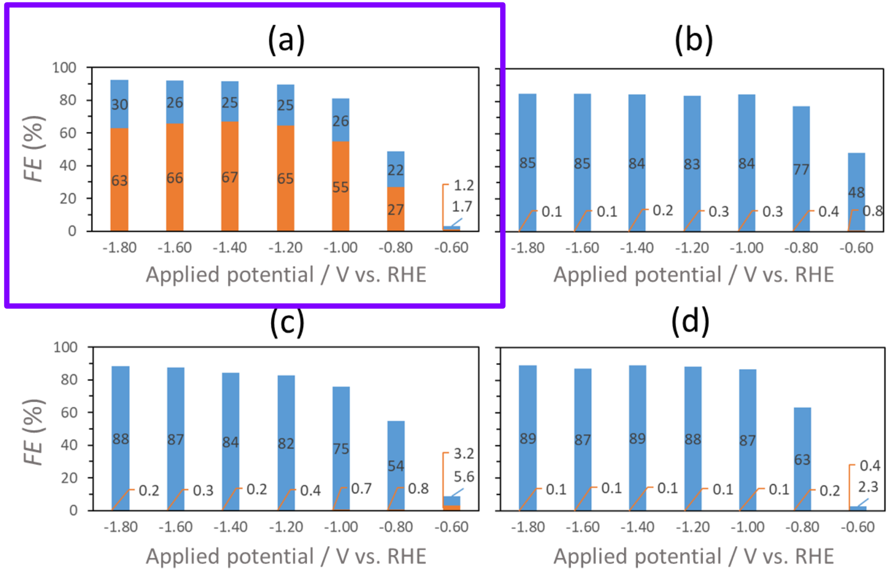


Figure 6. Applied potential dependence of Faradaic efficiency (FE) for CO2RR in 1.0M aqueous $KHCO_3$ solution using each cathode with (a) Zn-Al LDH, (b) Ni-Fe LDH and (c) Ni-Al LDH, and (d) without LDH. (**orange bar: CO**, **blue bar: H_2**)

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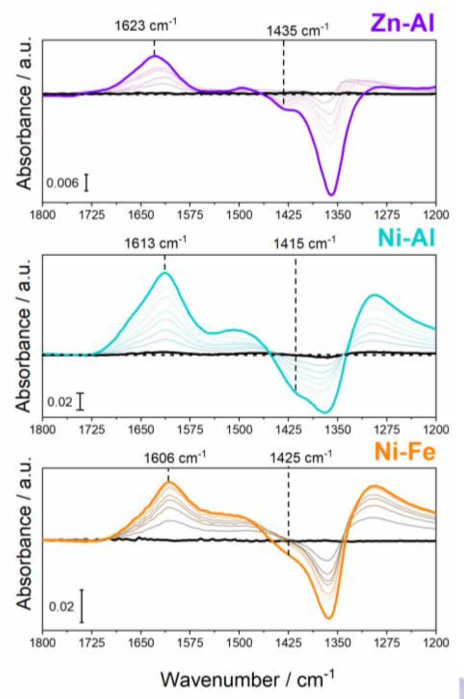
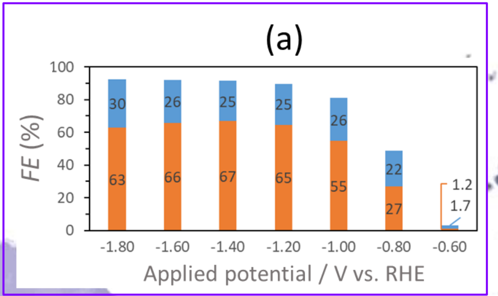
CONCLUSIONS

CONCLUSIONS



- The in situ **ATR-IR** measurements highlighted that the **three LDH** samples formed **different families of bidentate carbonates** with different strength and stability which are leading to a **different reactivity of the samples**.

- The Zn-Al LDH, which shows also a different carbonate evolution in in-situ ATR-IR measurements, exhibited the highest CO-forming CO2RR activity.



CONCLUSIONS

- Further development of Zn-Al LDH as a CO2RR catalyst.
    - **Currently under investigation different Zn-Al LDH** system, with different ratios of Zn-to-Al.

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THANK YOU FOR YOUR KIND ATTENTION

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