IR spectroscopy studies on Layered Double Hydroxides as possible electrocatalysts for CO_2 reduction reaction to CO

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Contents

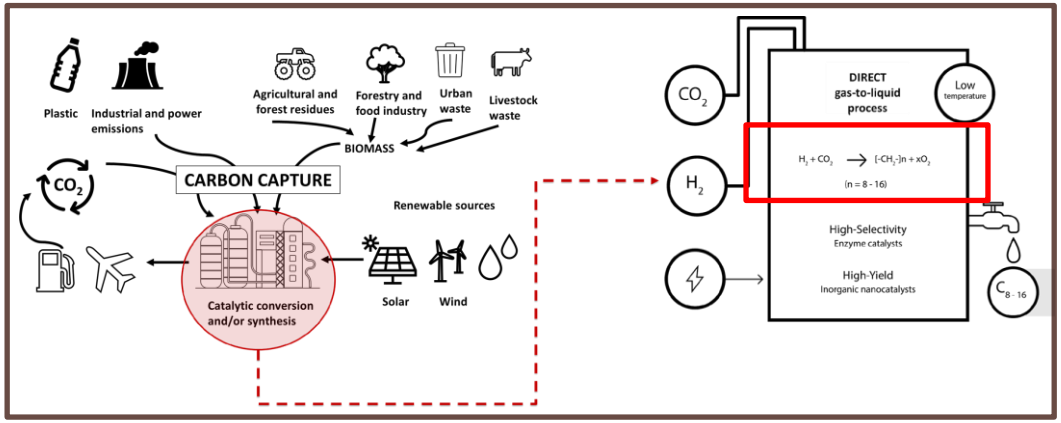
Introduction

1 Introduction

4AirCRAFT Project

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

4AirCRAFT combines **hybrid catalytic conversion** and **process intensification** to bring out an efficient, precise, flexible and scalable unique technology to **direct convert recycled CO_2** into sustainable and clean liquid fuels, thus making flying carbon neutral.



4AirCRAFT approach.

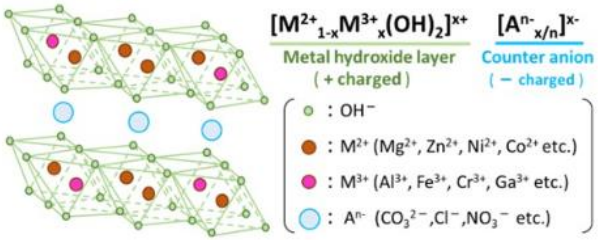
1 Introduction

Aim of the work

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

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.



Scheme of LDH structure.

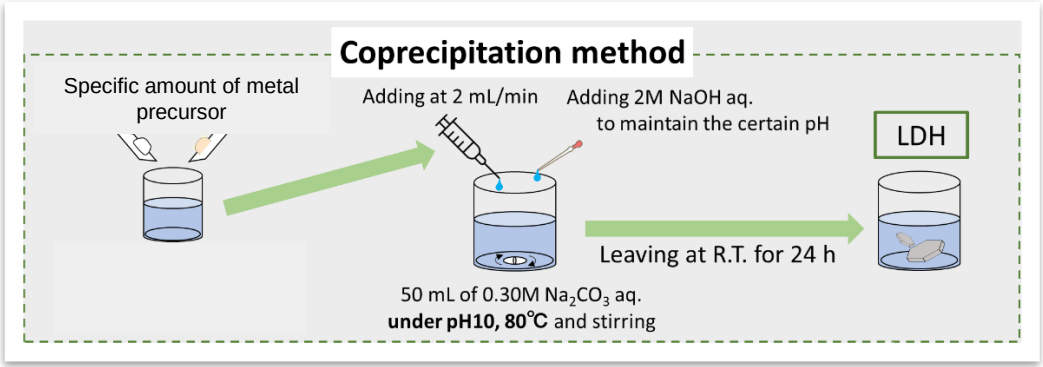
[1]X. Duan et al., *Adv. Mater.*, 29 (**2017**) 1701784.
[2]R. Nakazato et al. *RSC Sustain.* (**2023**), submitted.
[3]N. Yamaguchi at al. *J. Asian Ceram. Soc.* (**2023**), submitted.
[4]Y. Furukawa et al. *Solid State Ionics*., 192 (**2011**) 185–187.

2 Materials and methods

Materials and Methods

Synthesis procedure

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



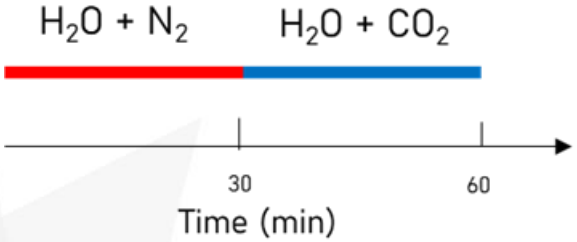
Three samples were studied:

- Zn-Al 1:2 → Best electrocatalytic performance
- Zn-Al 1:1
- Zn-Al 2:1

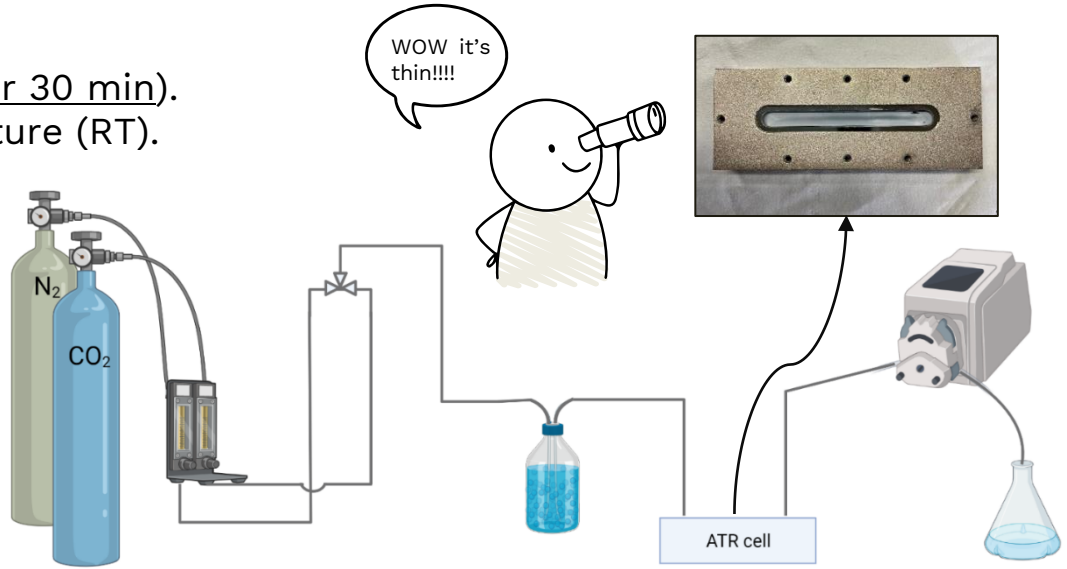
Materials and Methods

Methodology for IR experiments

- **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).



Scheme of the experiment performed

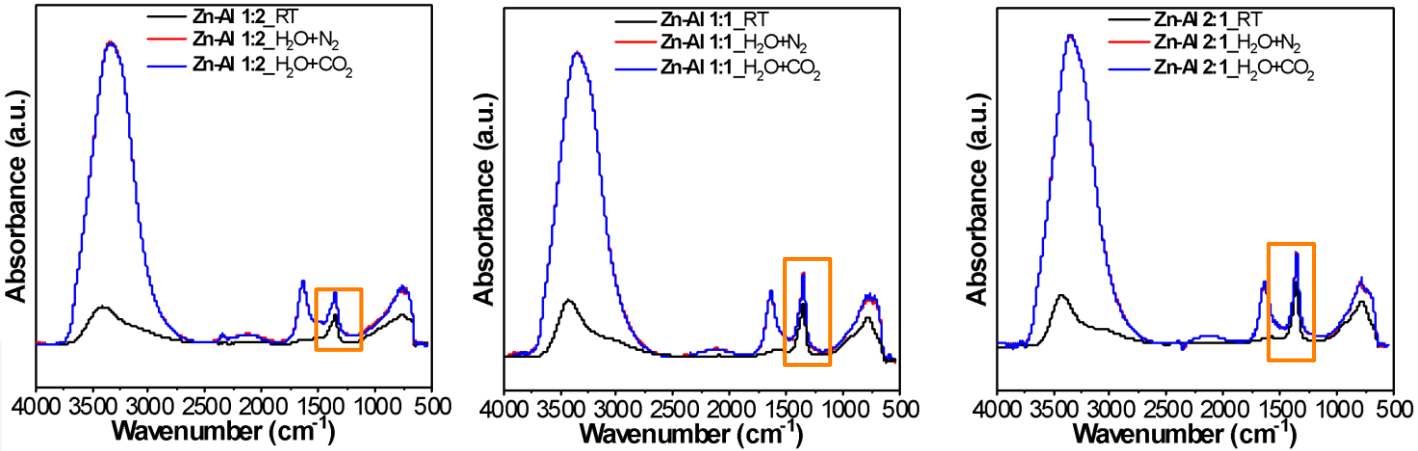


Set-up used for the FT-IR analysis.

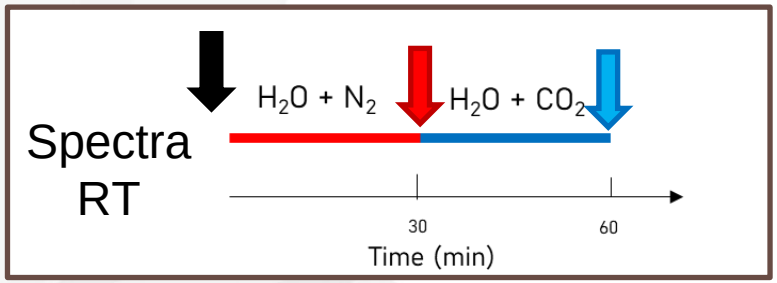
Results

3 Results

FT-IR results



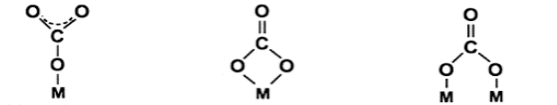
In situ ATR-IR spectra in the 4000-500 cm^{-1} spectral region of samples

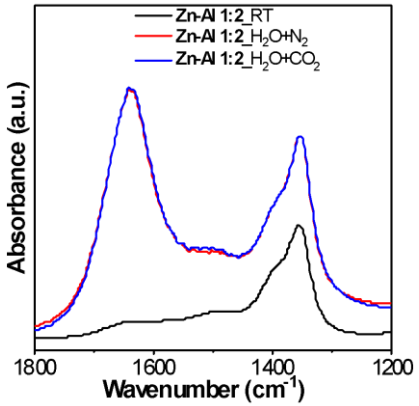


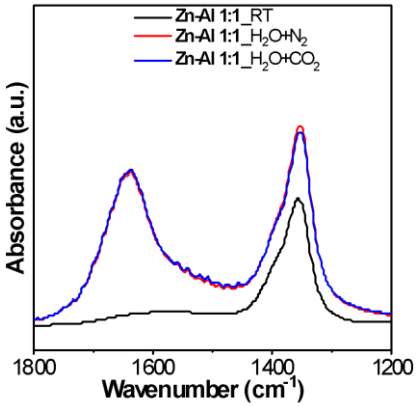
- The contact with H_2O caused an increase in the high frequency region bands associated to the **OH stretching**.
- The interaction of **CO_2** was responsible for the appearance of **surface** (**non-structural**) **carbonates-like species**.

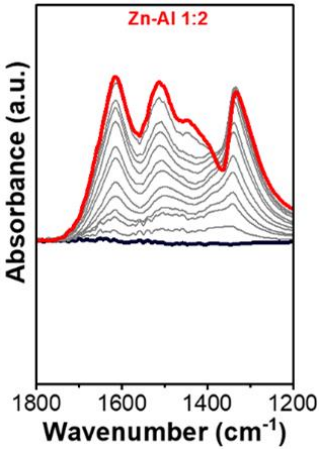
Results

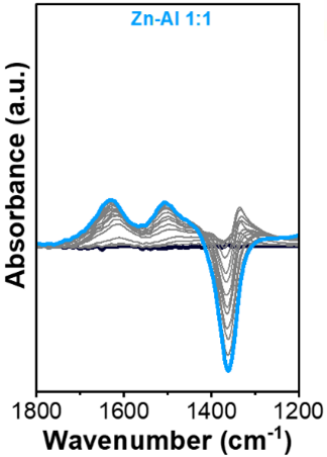
FT-IR results

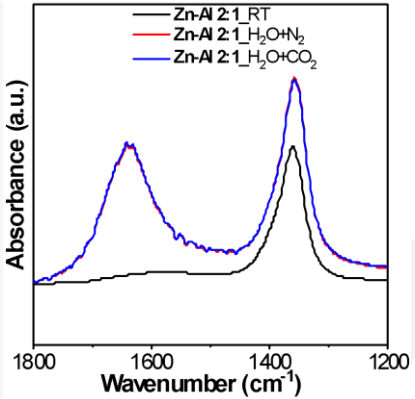


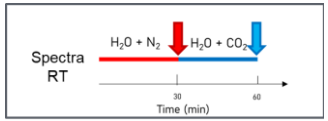


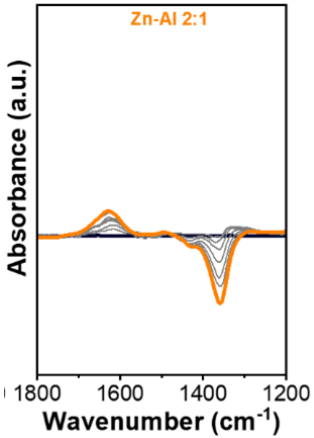








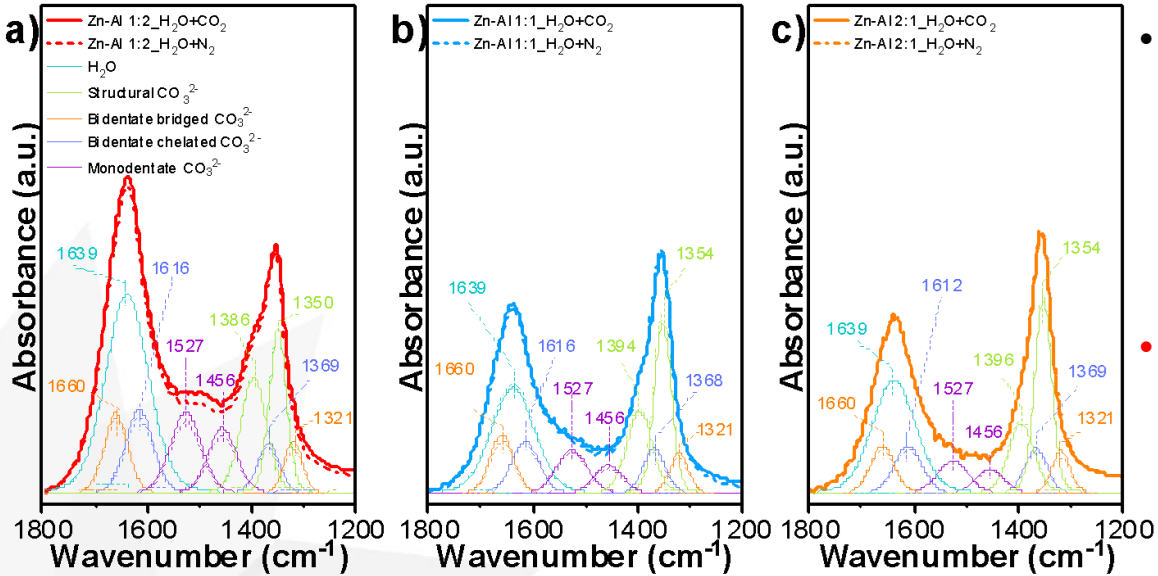




Spectra obtained by difference from those in the left side

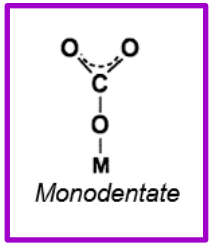
Results

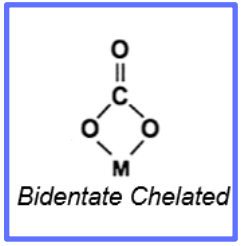
FT-IR results

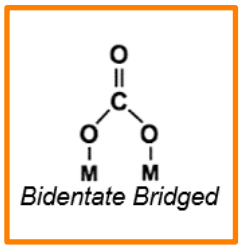


Deconvolution of carbonates species for **a) Zn-Al 1:2**, **b) Zn-Al 1:1** and **c) Zn-Al 2:1** in the range 1800-1200 cm^{-1}. The carbonates species are evidenced by different colours

- A **deconvolution** of the main families of carbonates was performed keeping the position of the structural interlayer H_2O and CO_3^{2-} fixed.
- **Different families of carbonates were evidenced**

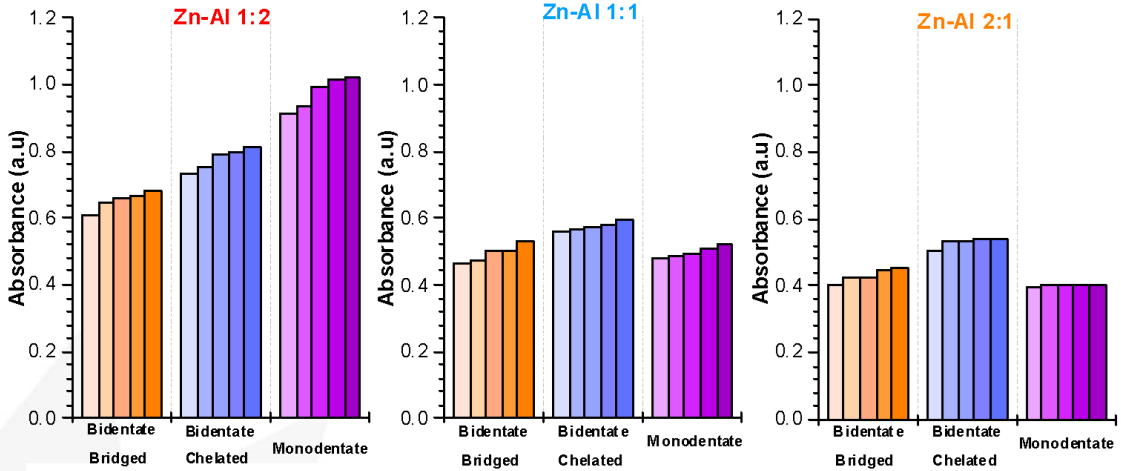




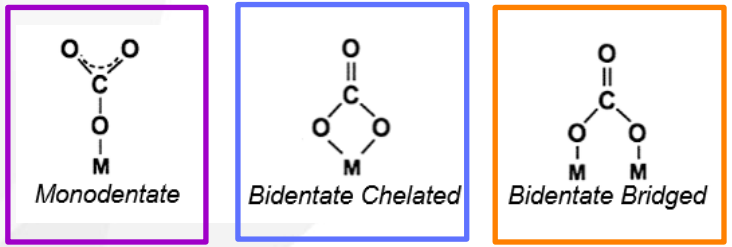


Results

FT-IR results



Evolution over the time of the different carbonates species



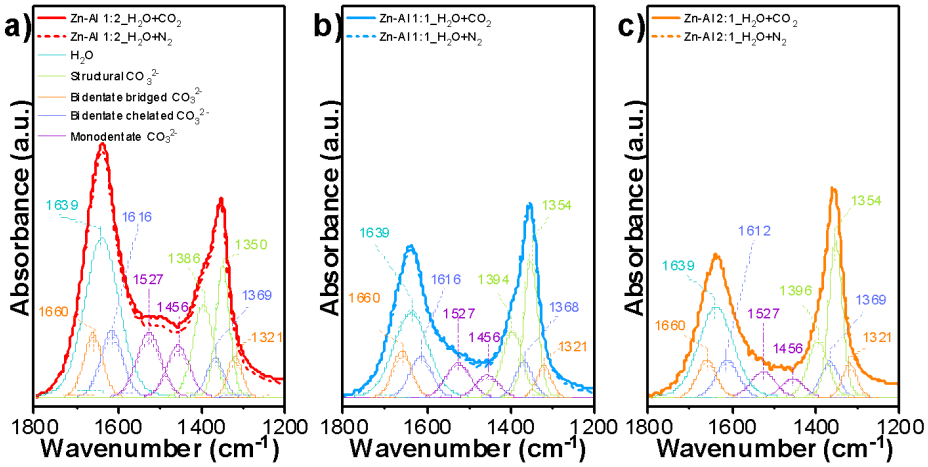
Zn-Al 1:2, compared to the other two samples, has higher number of monodentate carbonates species with respect to bidentate ones.

4

Conclusions and future perspectives

4 Conclusions and future perspectives

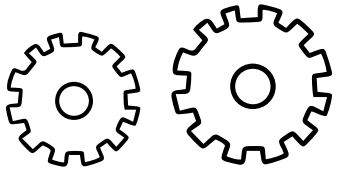
- The in situ **ATR-IR** measurements highlighted that the **three LDH** samples formed **different families of carbonates**.



4 Conclusions and future perspectives

- **The identification of the carbonate species was possible thanks to IR studies with cyclohexane** (for sake of brevity the results are not reported).

- The samples are currently under investigation for electrocatalytic tests by Hokkaido University.



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Thank you for your kind attention

Any questions?

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Supporting informations

Results

FT-IR results

- All the samples exhibit a **broad band** at **high wavenumbers** (3900-2500 cm^{-1}).
- In the **low frequency region**, there is the **overlapping** of the v2 out of plane of interlayer carbonate anions and the vibrational mode of lattice HO-M-OH and M-OH (450-800 cm^{-1}).
- In the **intermediate spectral region**, there is a band of the bending vibrations of the interlayer water molecules, and the asymmetric v3 stretching mode of the structural interlayer carbonates at around 1400 cm^{-1}.

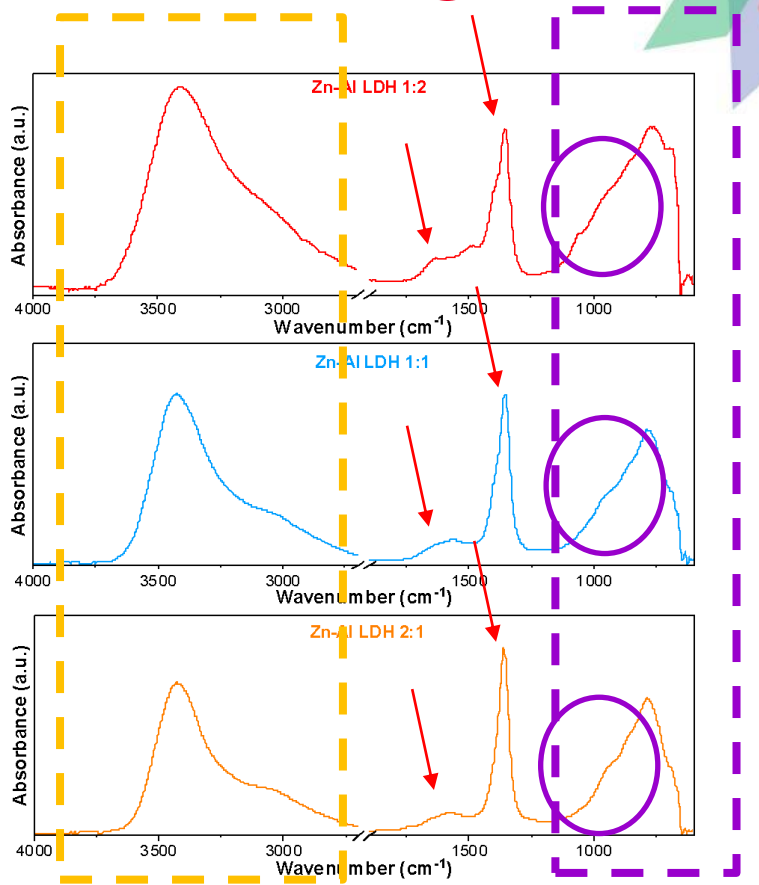
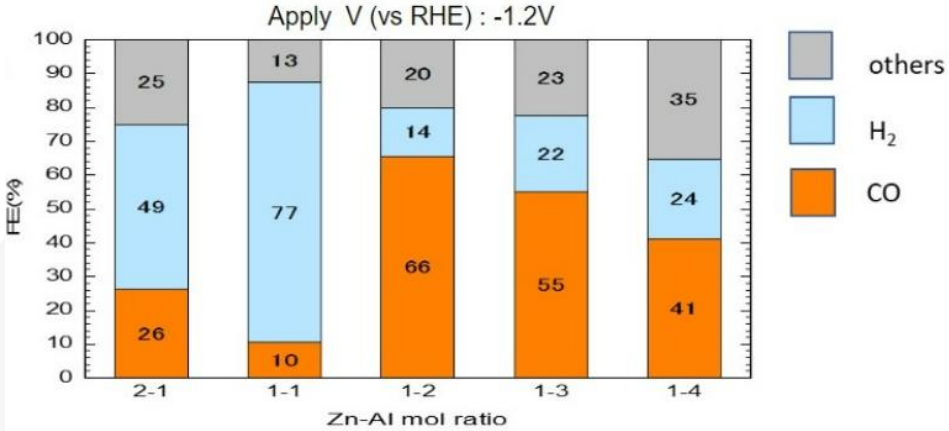


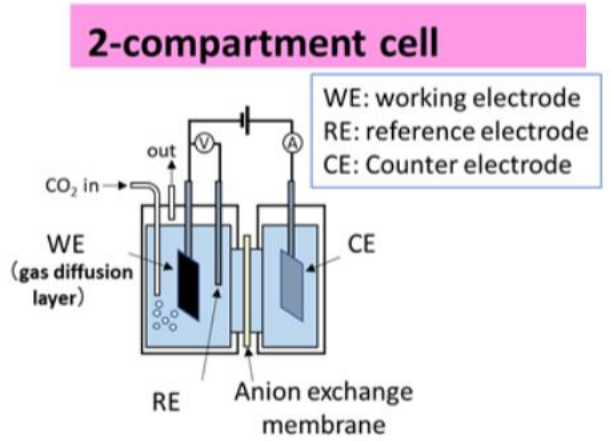
Figure 4. ATR-IR spectra in the 3700-650 cm^{-1} spectral region of dry Zn-Al LDH samples.

Results

Preliminary Electrocatalytic results



Applied potential dependence of Faradaic efficiency (FE) for CO2RR using each cathode with different Zn-Al molar ratios.



Dissolved CO_2RR

✓ **Factors to limit the CO2 RR reaction**

Saturation concentration of CO_2 (33 mM)

Diffusion rate of CO_2

Limit of electrolyte because of dissolution of CO_2