MOF/CNT nanocomposites and their carbonisates for catalytic application: synthesis and characterisation

Agata Łamacz[1*], Marcin Markiewicz[1], Tomasz Jędrzejewski[1], Maciej Róziewicz[1], Paweł Stelmachowski[2], Izabela Janowska[3]

[1] Wroclaw University of Science and Technology, Poland
[2] Jagiellonian University, Kraków, Poland
[3] Strasbourg University (CNRS), France
* agata.lamacz@pwr.edu.pl

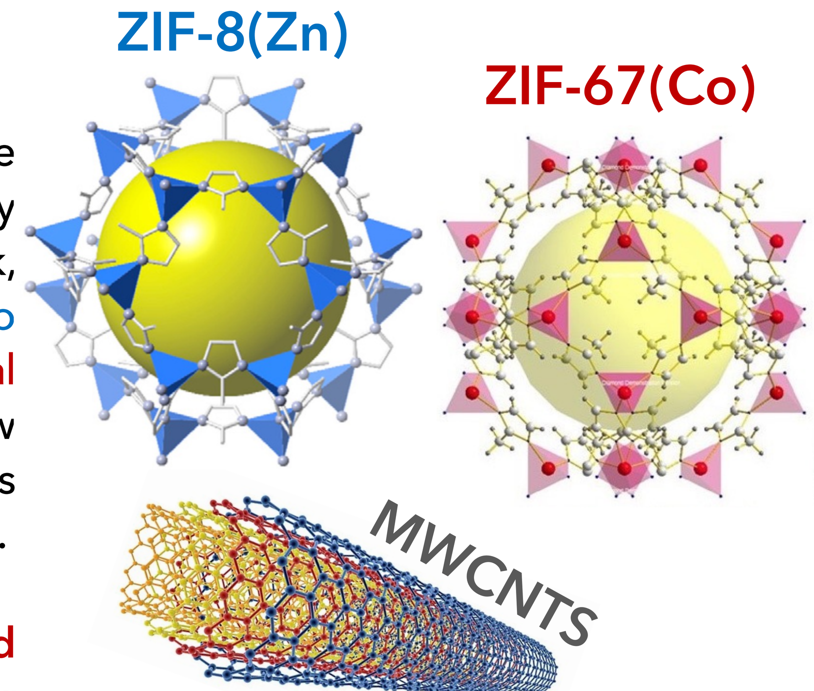
Wrocław University of Science and Technology

Carbon 2023 · Cancun Mexico · The World Conference on Carbon

INTRODUCTION:

The imidazole zeolite framework (ZIF) has attracted widespread attention due to its high surface area, large pore volume, and unique advantage of easy functionalization. Owing to the presence of Zn^{2+} ions in the framework, modified with Cu ions ZIF-8 can be used as a catalyst in CO_2 hydrogenation to MeOH. While ZIF-67(Co) has been considered an interesting electrode material with excellent performance in oxygen evolution reaction (OER) providing a new approach water electrolysis. Combining both ZIFs with other materials, such as CNTs, can be also advantageous for their stability and (electro)catalytic activity.

The aim of this work was to obtain Cu modified ZIF-8 and Ni+Fe modified ZIF-67 composites with CNTs (and their carbonisates) and to determine their performance in MeOH synthesis and in OER.



Y-R. Lee et al. Chem. Eng. J. 271 (2015) 276.
D. Matatugi et al. Proceedings 1 (2017) 462.
Angel Soler Gollonet/shutterstock.com

CATALYTIC TESTS – MeOH SYNTHESIS

- T=200°C, p=18 bar
- Feed: H_2/CO_2=3/1
- Non-gradient flow-reactor

ELECTROCATALYTIC TESTS – OER

Cell Characteristics:

- Reference Electrode: Hg/HgO in NaOH (1 M)
- Counter Electrode: Pt wire
- Working Electrode (our samples)
- rotating disc electrode, R=1600 rpm, d=3 mm
- Atmosphere: Ar gas saturated

Electrolyte:

- 50 mL KOH (0.1 M, pH~13)

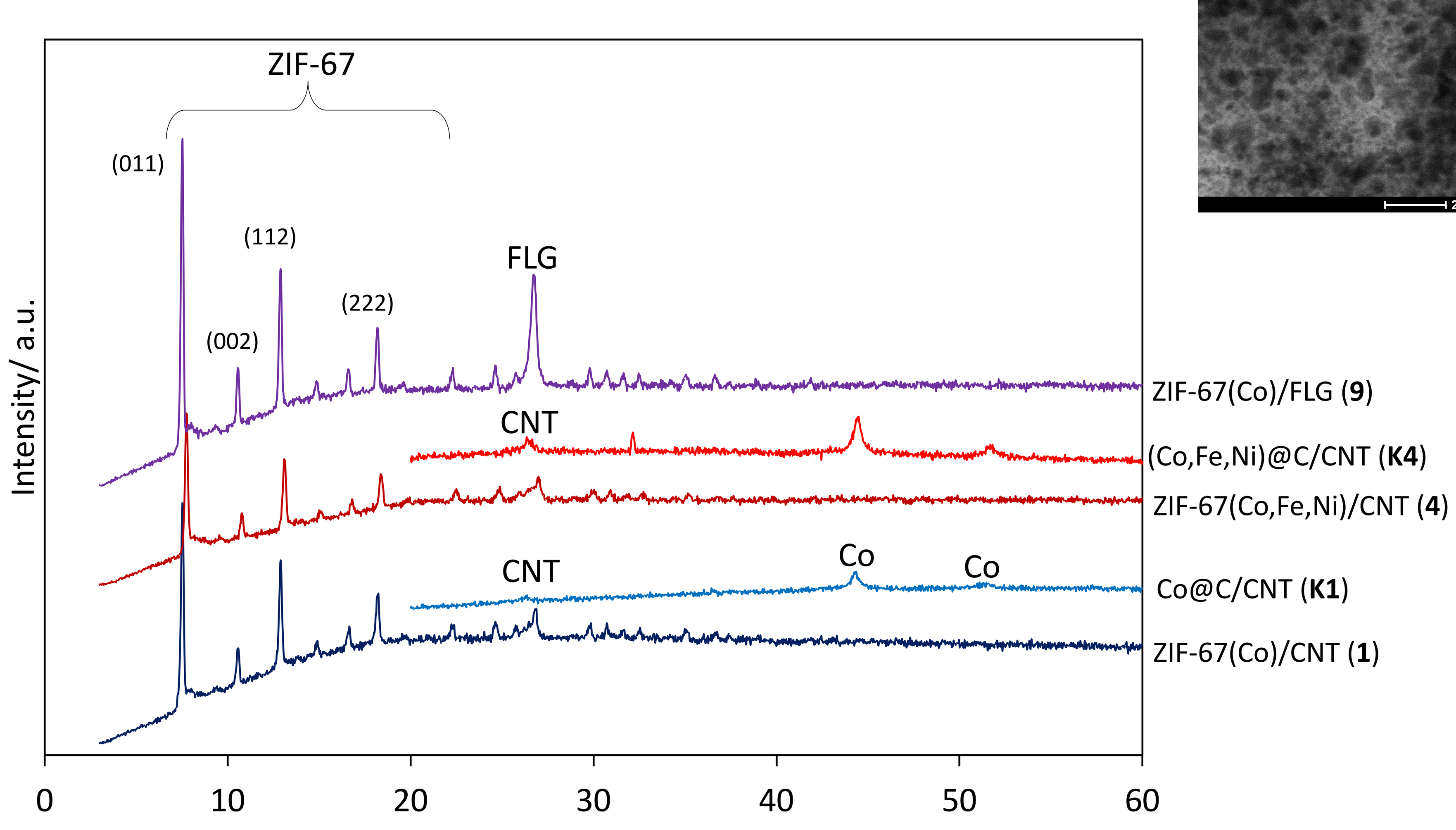
RESULTS - MeOH synthesis: $CO_2 + 3H_2 = CH_3OH + H_2O$

Compared to conventional supported Cu/ZnO catalysts, the selectivity to MeOH and STY are significantly higher over the ZIF-8 containing samples:

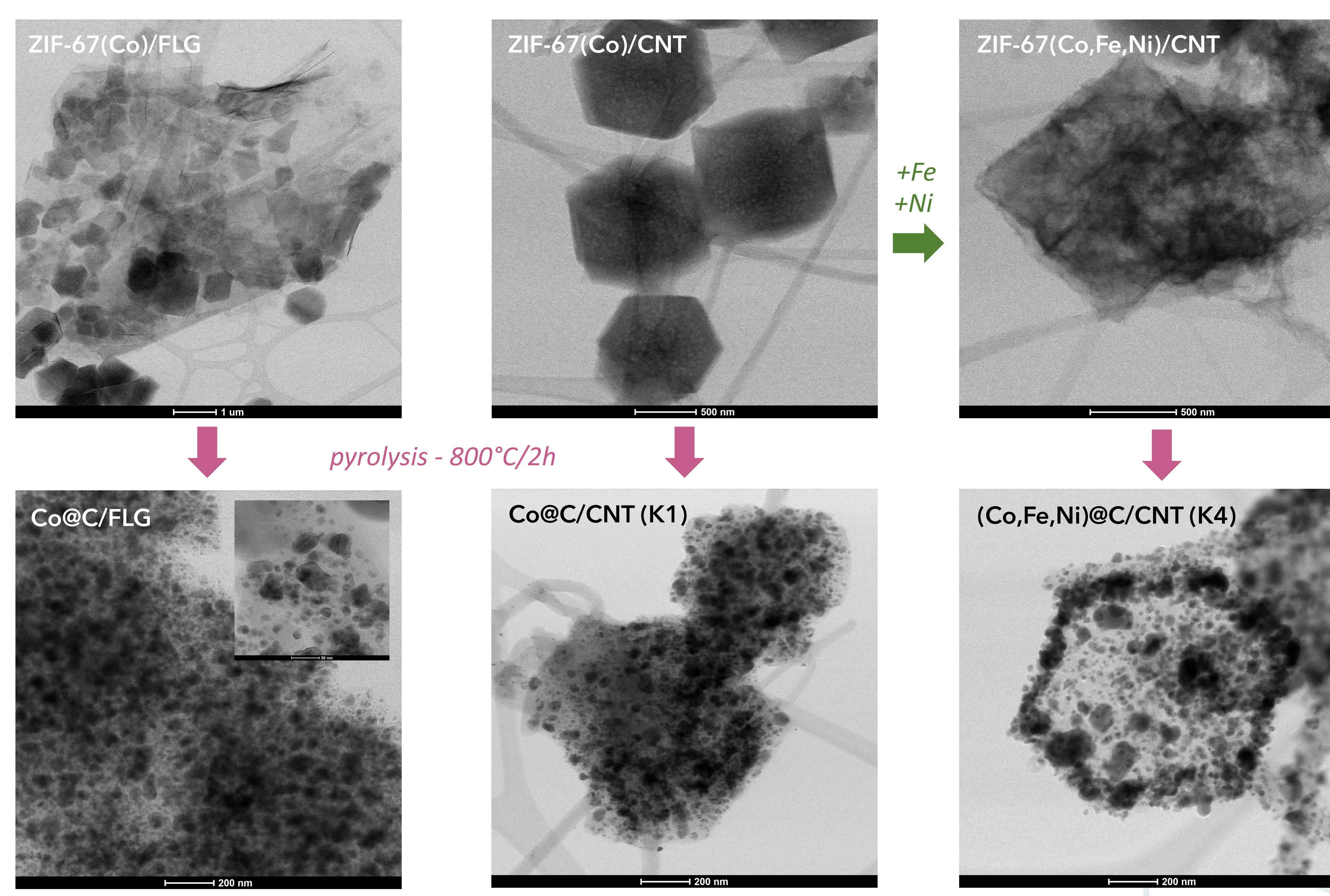
CATALYST	Selectivity to MeOH (%)	STY ($mmol_{MeOH}/g_{Cu}/h$)
$Cu/ZnO/Al_2O_3$ [1]	47	3.1
$Cu/ZnO/ZrO_2$ [2]	41	3.8
ZIF-8(Zn)	92	-
Cu/ZIF-8(Zn)	90	123.5
(Cu,Zn)@**C** [a]	88	13.6
ZIF-8/**CNT**(Cu,Zn) [b]	98	83.1
(Cu,Zn)/**CNT** [c]	93	9.2

[a] 17 wt.% CuO + 33 wt.% Zn+ 50 wt.% C
[b] 5 wt.% Cu + 85 wt.% ZIF-8 (40 wt. % Zn) + 10 wt.% CNT
[c] 15 wt.% CuO + 60 wt.% ZnO + 25 wt.% CNT

[1] *Levalant et al., J. Catal. 324 (2015) 41*
[2] *Xiao et al., Appl. Surf. Sci. 338 (2015) 146*

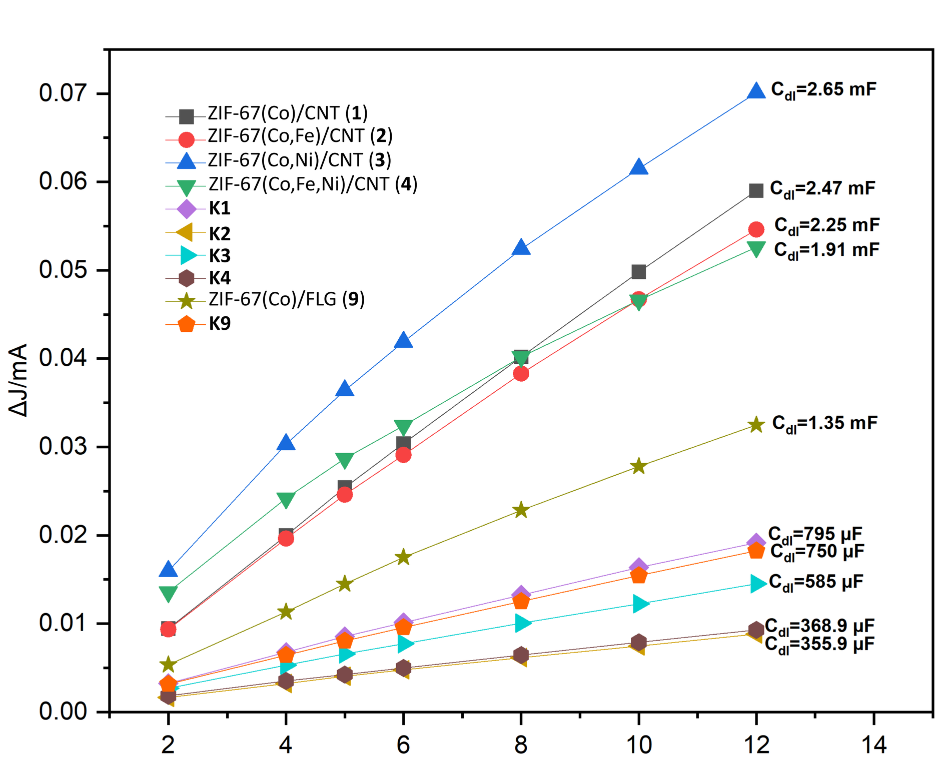


RESULTS – Oxygen Evolution Reaction

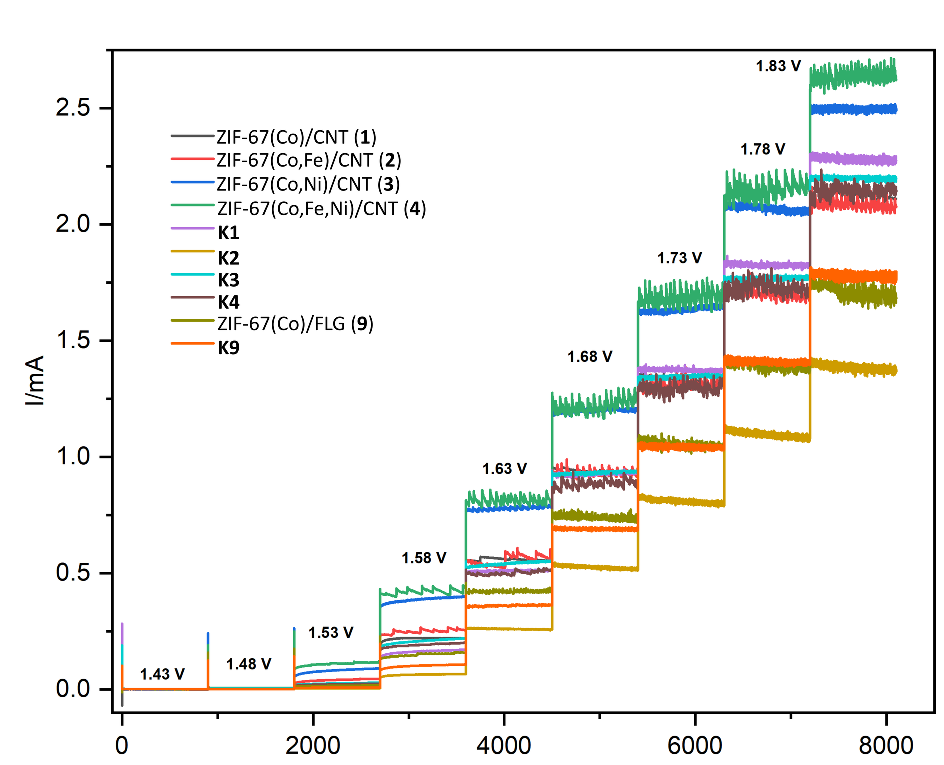


ZIF-67(Co,Fe,Ni)/CNT: 20 wt.% ZIF-67(Co), 2 wt.% Fe, 16 wt.% Ni, 62 wt.% CNT
(Co,Fe,Ni)@C/CNT: 6.1 wt.% Co, 2.1 wt.% Fe, 17 wt.% Ni, 9.2 wt.% C, 65.6 wt.% CNT

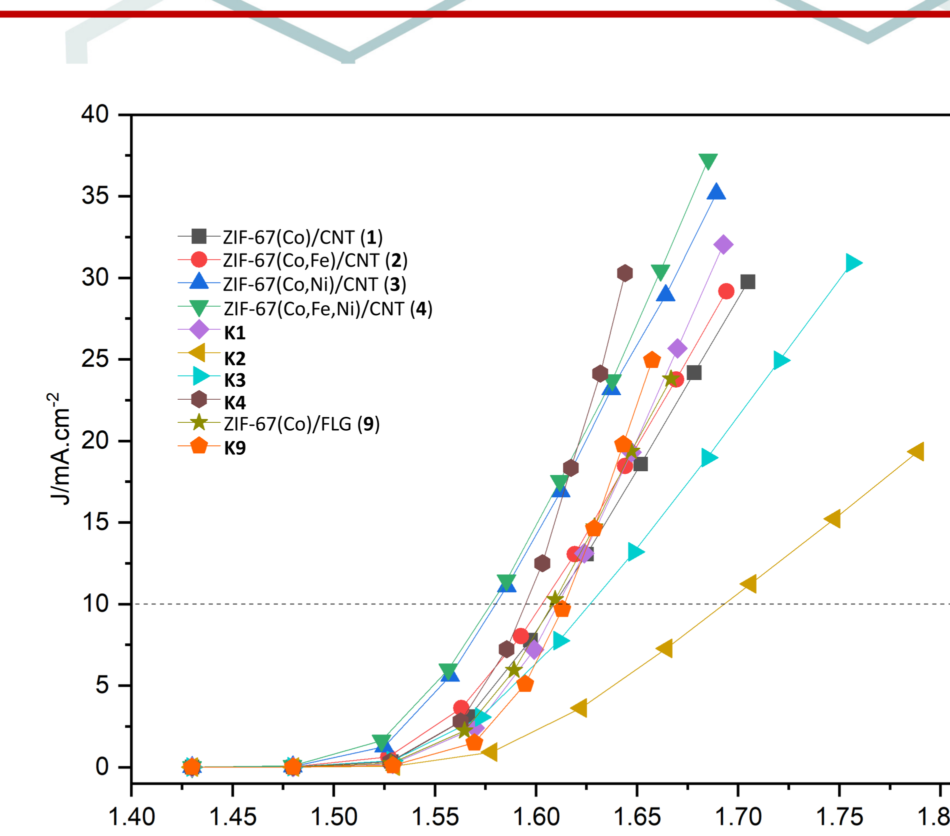
- **ZIF-67(Co,Ni)/CNT and ZIF-67(Co,Fe,Ni)/CNT show the best performance in OER.**
- The activity of ZIF-67(Co,Ni)/CNT increases in time = the sample undergoes some activation.
- The addition of **Fe does not improve the electrocatalytic activity of the samples.**
- The overpotential for the most active samples is ca. 350 mV - sufficiently good.
- All samples show stable behaviour during the test.
- **Carbonisation deteriorates the activity in OER (decrease of electrocatalytically active surface).**



Double layer capacitance results.



Chronoamperometric reactivity tests in the oxygen evolution reaction.



IR-corrected reactivity in oxygen evolution reaction.

Acknowledgement: The research was financed by the National Science Centre – grant no. 2019/35/D/ST5/03440.