CO2-based electrosynthesis of Ethylene oXIDE

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15th International Meeting ISSFIT-2020

30 November – 6 December 2020, Chernogolovka, Russia

Electro-catalytic reformation of CO_2: catalysts for $CO_2 \rightarrow C_2H_4$ reaction promotion

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CO_2EXIDE-Project

- **Aim:** The establishment of an electrochemical, energy efficient and near-to CO_2-neutral process for the production of the bulk chemical ethylene oxide from CO_2, water and renewable energy.
- **Duration:** January 2018 – December 2020
- 3-years funding by **Horizon2020**

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768789.

Ten partners in six countries

ACADEMIC CENTRE FOR MATERIALS AND NANOTECHNOLOGY AGH	Development of CO_2 reduction catalyst
axiom	CO_2 feedstock preparation, CO_2 recovery from biogas, ethylene enrichment, ethylene separation
MŰEGYETEM 1782	Electrolysis parameters, stable operating conditions, catalyst stability, contaminants, surface analyses
ENERGIE INSTITUT an der Johannes Kepler Universität Linz	Life Cycle Assessment, Techno-economic process and product assessment
EPC	Communication and dissemination, coordination support
Fraunhofer IGB	Coordination, electrocatalytic oxidation reaction, ethylene oxidation, chemical conversion
LATVIJAS UNIVERSITĀTES CIETVIELU FIZIKAS INSTITŪTS	Cathode, catalyst modified multi-layer graphene stacks, theoretical calculations, electrolysis half-cell with gas monitoring, Polymer SPEEK / ionic liquid composite
SCHAEFFLER	Nanostructured coatings for catalyst, coating process development
SIEMENS Ingenuity for life	Electrochemical cell design, system integration, scale-up, testing and validation
UNIVERSITY OF Southampton	3D printed electrodes; anodic hydrogen peroxide; carbon dioxide reduction; flow cell, gas diffusion electrodes

CO_2EXIDE-Progress

Mth 1-12

- CO2 reduction
- H2O oxidation
- Ethylene oxidation with H2O2

Mth 13-24

- Electrocatalytic reactor
- Gas separation
- Chemical Conversion

Mth 25-36

Assembling and testing

coordination, management, risk analysis and contigency planning

dissemination, transfer and exploitation

CO_2EXIDE-Technology

Renewable sources (e.g. biogas)

Renewable electricity

Water

CO_2

C_2H_4

Cathodic reaction

Simultaneous Electrocatalysis

Anodic reaction

H_2O

H_2O_2

Separation and chemical conversion

C_2H_4

C_2H_4O

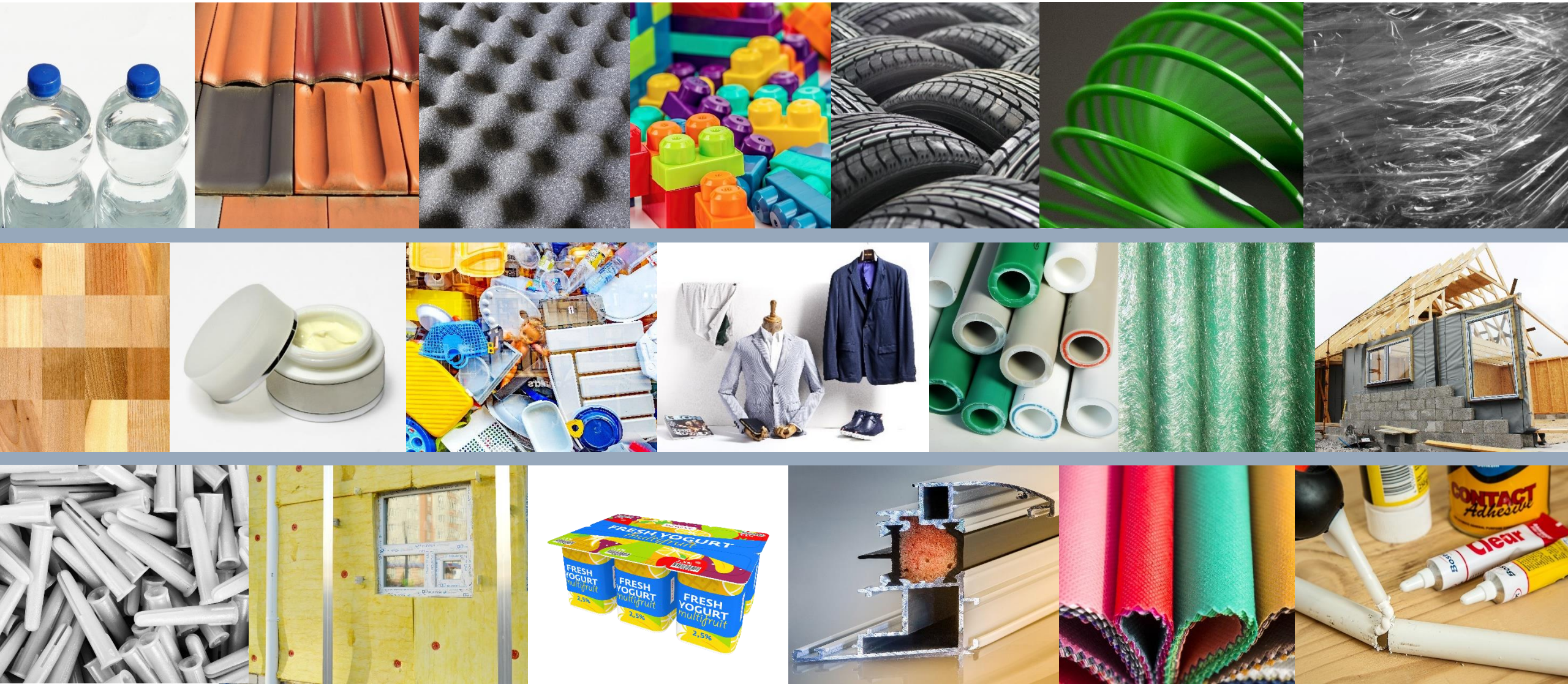
H_2O_2

PET

Oils and fats (green liquid fuels)

… and many more products

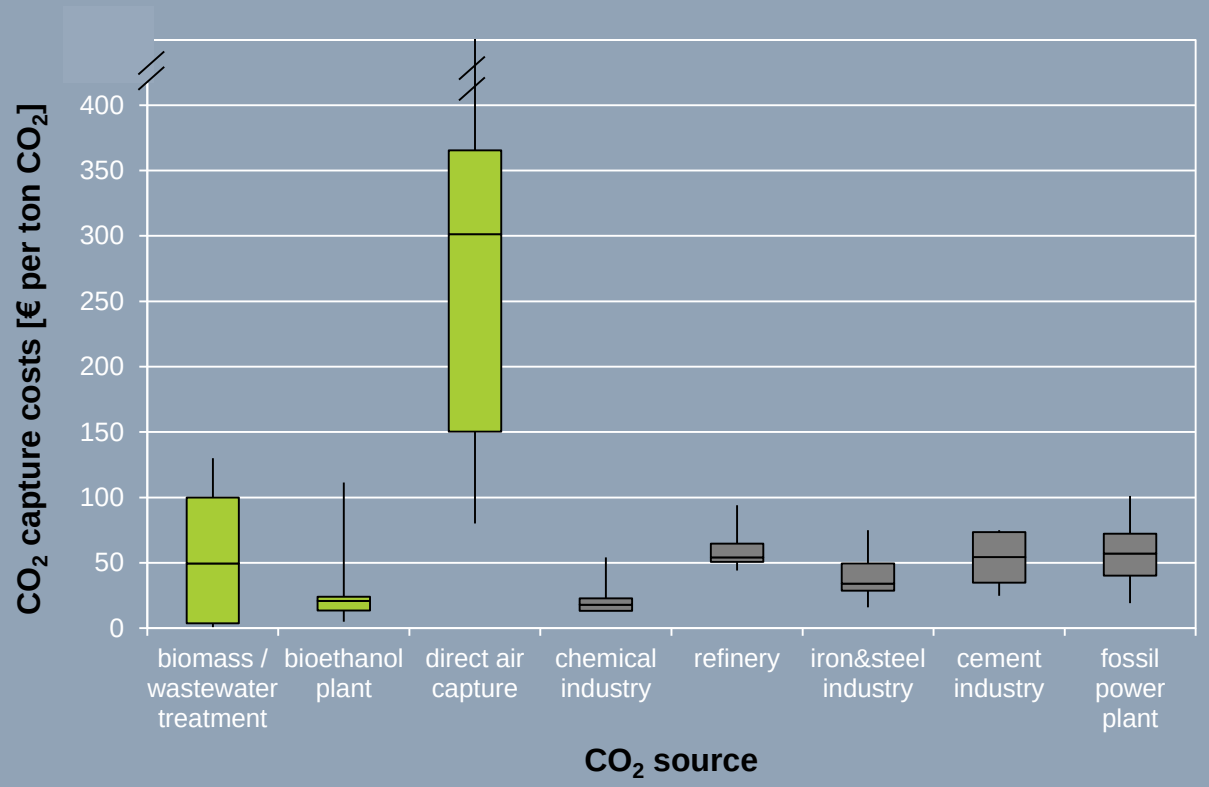
The bulk chemical Ethylene Oxide



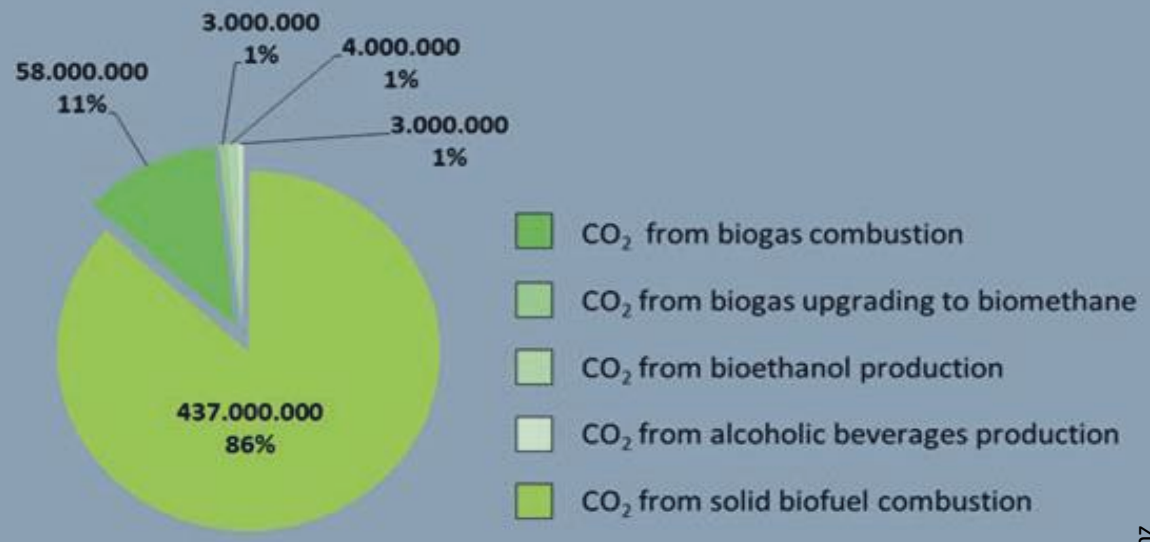
CO_2-Capture

CO_2 capture costs

- CO_2 from **biogenic sources** can provide **lowest capture costs**
- **Direct Air Capture** (DAC) is expected to rapidly **reduce its costs**



Biogenic CO_2 in Europe [tons/year]



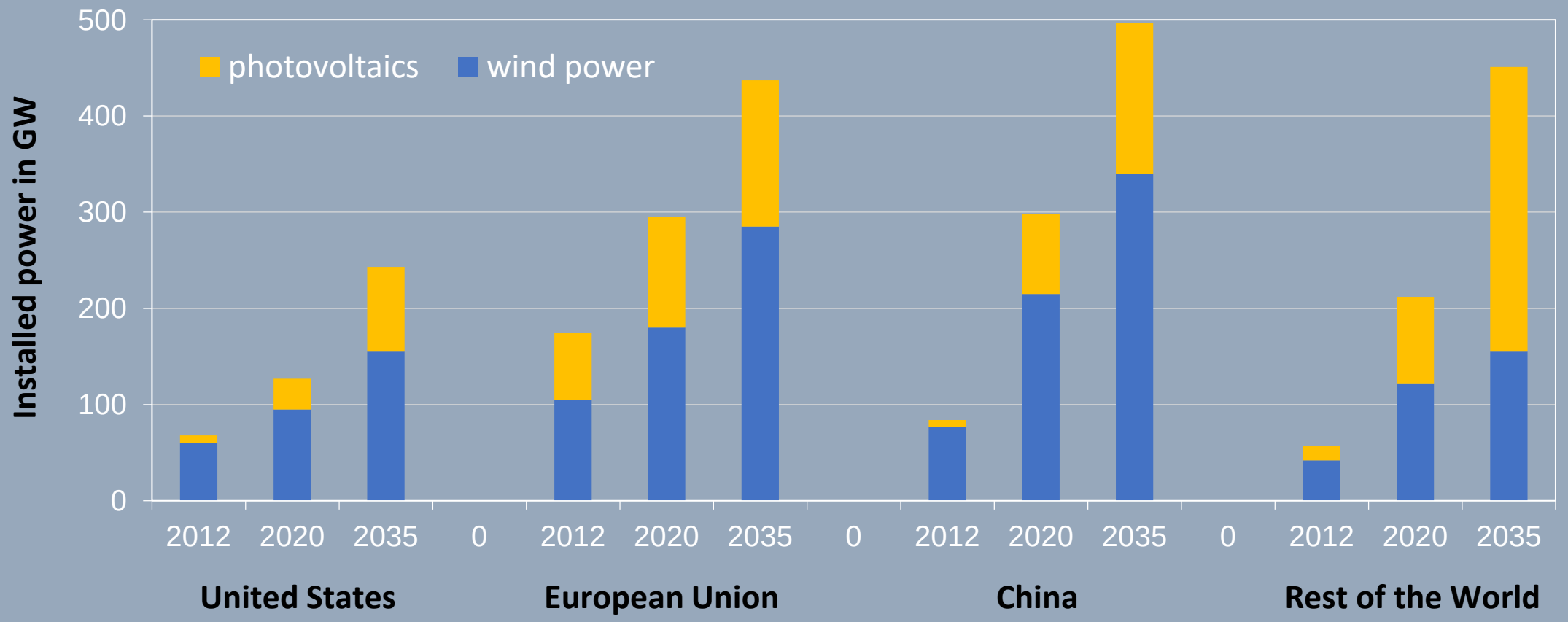
Total: **approx. 506 Mio tons / year**

Global demand of ethylene (C_2H_4): **125-150 Mio tons / year**

→ A conversion of the biogenic exhaust gas of Europe could meet the annual demand worldwide.

Source: Energieinstitut Linz

Europe‘s renewable electricity production is growing



Source: data based on IEA (2013) World Energy Outlook

Central Innovations

- Simultaneous catalysis
- Integrated conversion
- Development of electrochemical catalysts and electrodes
- PEM-Cell
  - compact design
  - small thermal inertia
  - dynamic operation mode

Impact of the CO_2EXIDE-Technology

1. **Mitigating climate change by CO_2-utilization**
   Biogenic CO_2 as primary carbon source
2. **Generating renewable resources**
   Substituting conventional fossil-based ethylene oxide production and related emissions
3. **In line with renewable energies**
   Feasible for fluctuating renewable electricity and decentralised production sites

The electrochemical synthesis could save up to **100% of GHG emissions and** at least **25% of the energy demand** related to the conventional production of ethylene oxide and hydrogen peroxide

Partner in Latvia

Cathode, catalyst modified multi-layer graphene stacks, theoretical calculations, electrolysis half-cell with gas monitoring, Polymer SPEEK / ionic liquid composite

Institute of Solid State Physics, University of Latvia

Present days

In 2001 - Excellence Centre of Advanced Material Research and Technology (CAMART), an EU project developed by the ISSP UL with mission to promote research and disseminate knowledge of modern functional materials and technologies.

In 2017 - CAMART2 – Centre of Advanced Materials Research and Technology Transfer. Consortium partners – KTH Royal Institute of Technology and Acreo Swedish ICT. Horizon 2020 financial support up to 15 MEU'. "Strategy ISSP UL 2016 – 2026" - research, development and innovations at the World level; world-class scientists, Open Access Laboratories etc.

Participants in project from ISSP

JK group – Laboratory of Materials for Energu Harvesting and Storage (Janis Kleperis)

JZ group - Laboratory of Computer Modeling of Electronic Structure of Solids (Jurijs Žukovskis, Sergejs Piskunovs)

GV group – Laboratory of Chemical Technologies (Guntars Vaivars)

JP group – Thin Film Laboratory (Juris Purāns)

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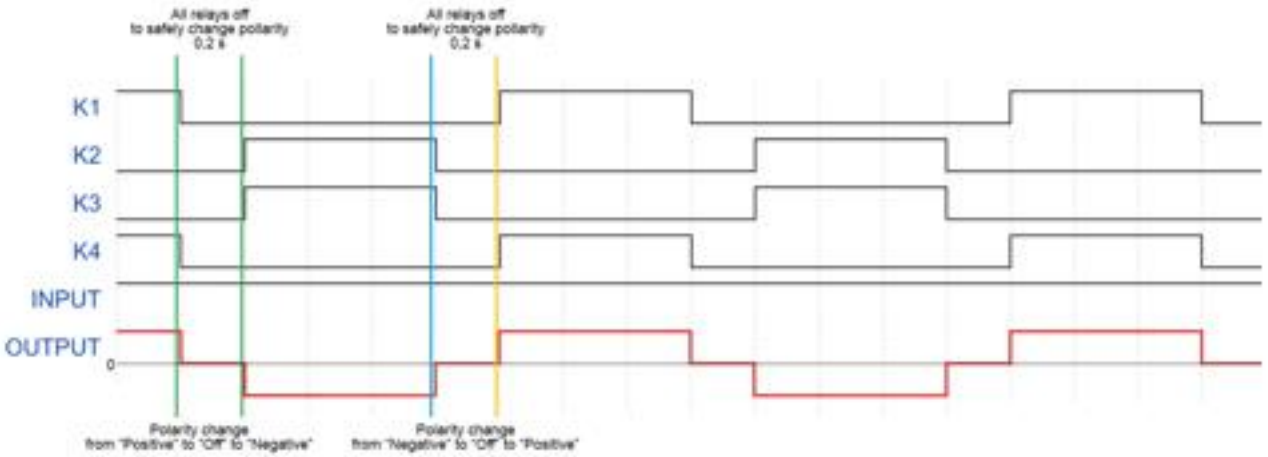
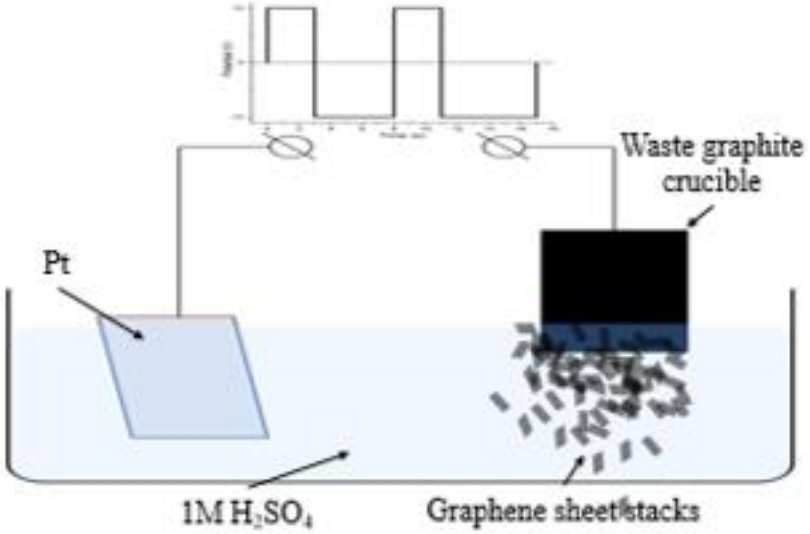
Conception of cathode material





Washing, splitting

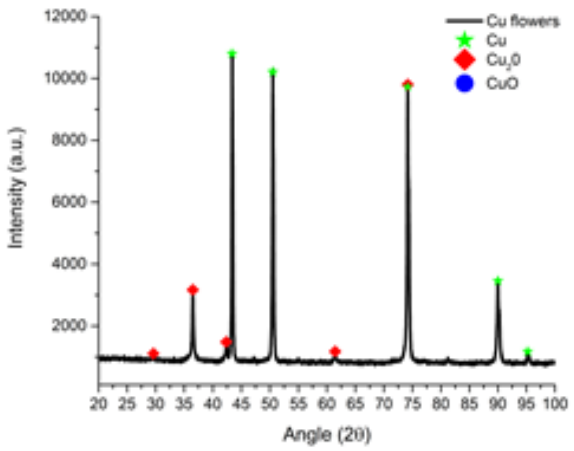
Reduction 700 °C; Ar/H_2

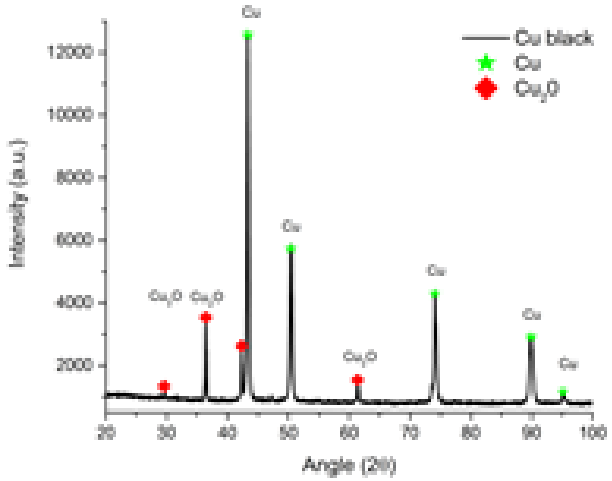
- Electrochemical exfoliation of graphite using a variety of electrolytes and a pulsed power supply unit.
- A novel pulse modulation circuit is being created.

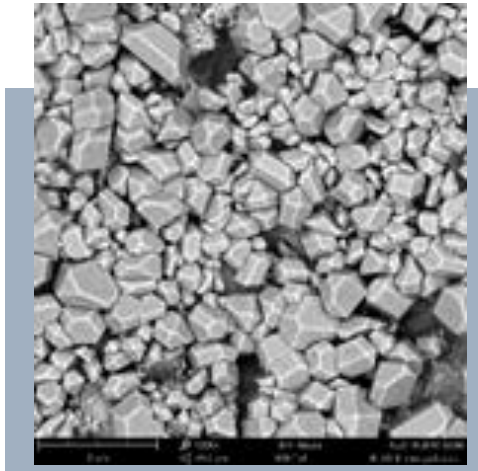
Material available for sharing

Coating GSS on CP with copper

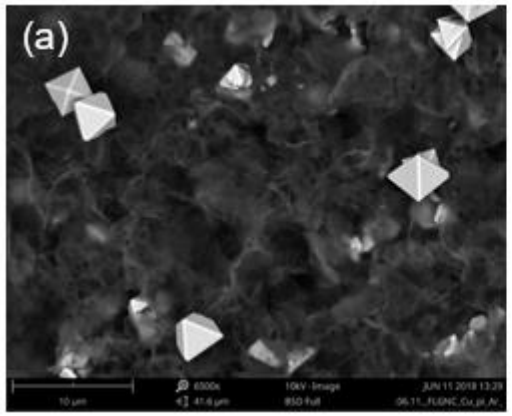
XRD, SEM investigation of deposited Copper structures on Cu foil

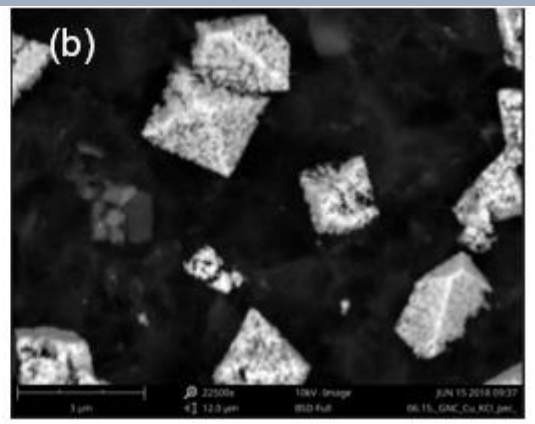






XRD measurements show that flower like structures and crystals are mostly Cu_2O.





a) Copper crystals before electrolysis

b) Copper crystals after electrolysis

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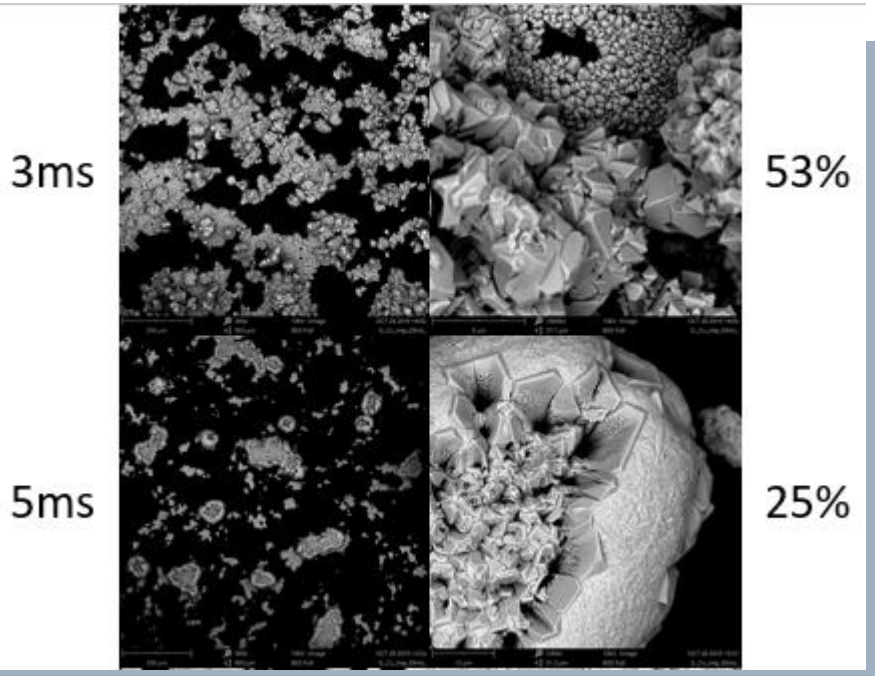
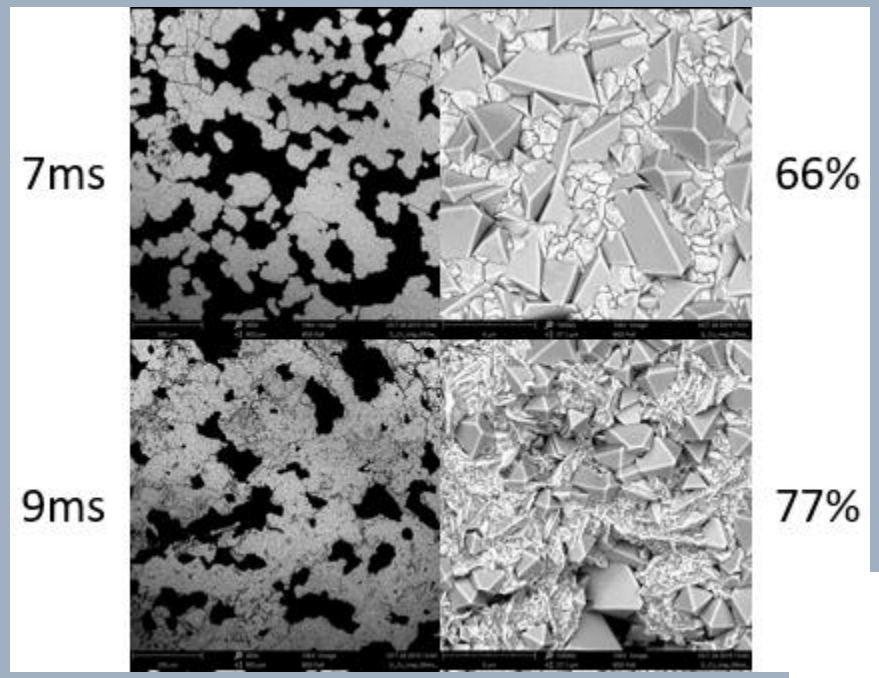
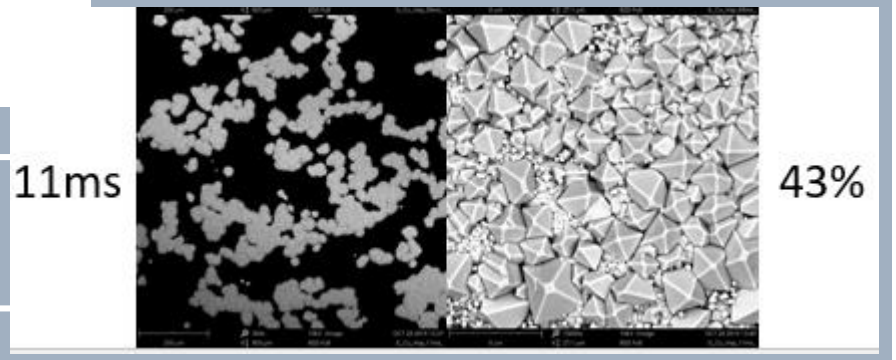
ISSP – Cu/Cu_2O catalyst layer – electrochemical pulse deposition on Fr-GDE in 1.25M $CuSO_4$

Cu/Cu_2O catalyst layer – Impact of pulse length on coating coverage density



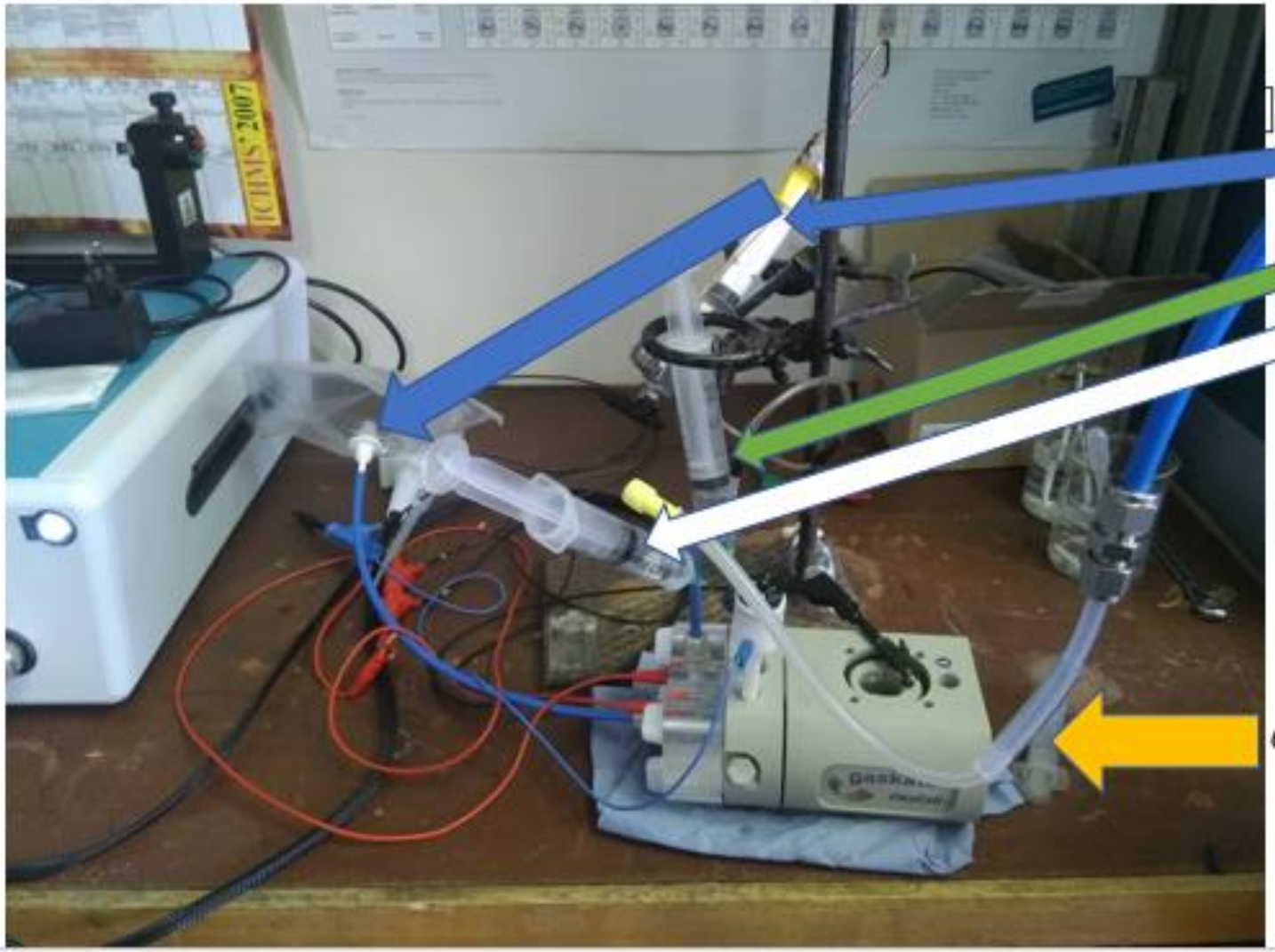




Pulse length, ms

Coverage, %

Cathode tests in FLEXCELL GDE/GSS/Cu tests



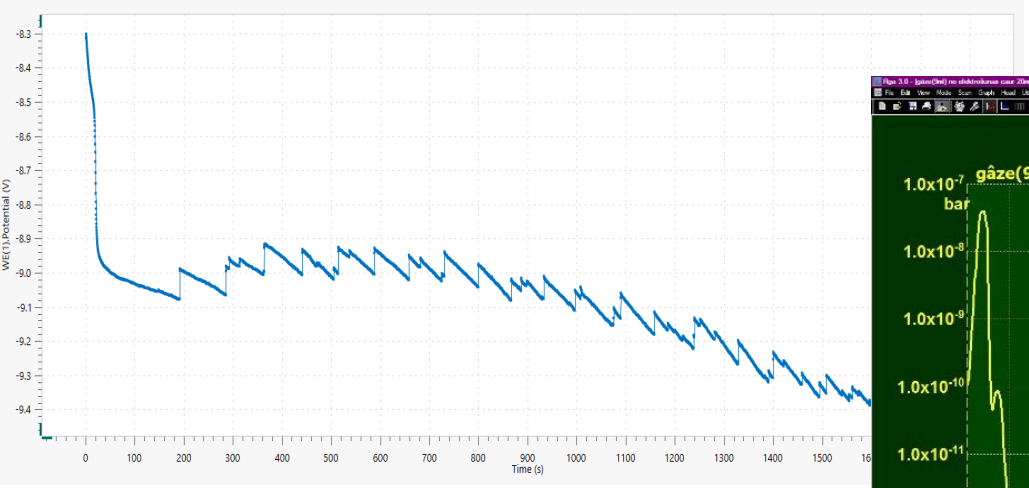
(1) for gas removal
(2) for filling with electrolyte
(3) for removal of excess air

Gaskatel cell;
Electrolyte: 0.5M $KHCO_3$;
Anode: Platinum;
Cathode: Carbon paper impregnated with GSS and electrodeposited copper
FUMAPEM membrane

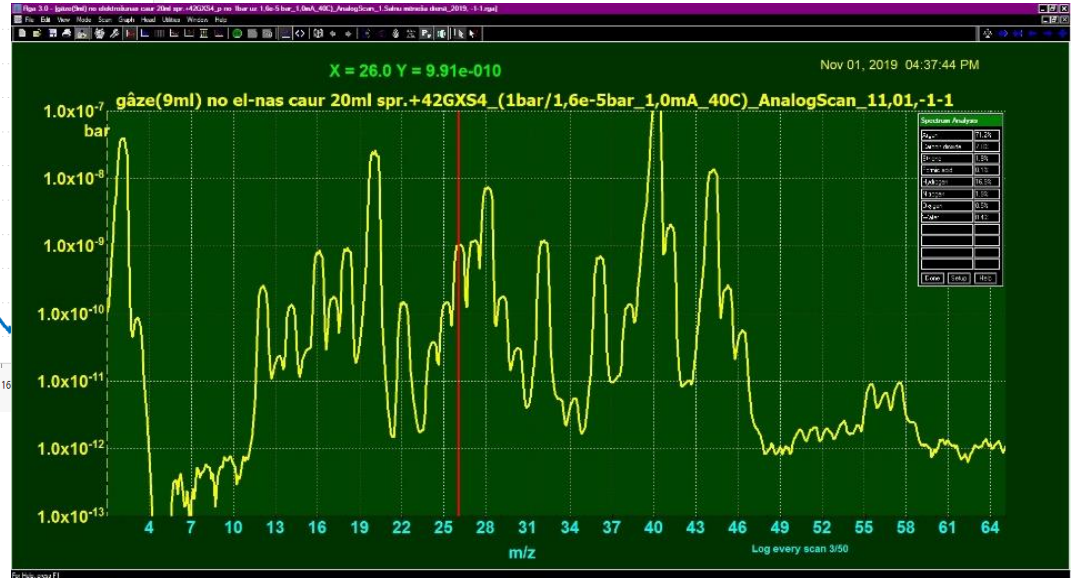
CO_2 flow through cathode

ISSP – Cu/Cu_2O catalyst layer – electrochemical pulse deposition on Fr-GDE in 1.25M $CuSO_4$

Cu/Cu_2O catalyst layer –tests in 1M $KHCO_3$; 150 mA/cm^2; 30 min



Change of cathode potential



For the first time, such a pronounced C_2H_4 spectrum was observed

Two tests 30 min with different CO_2 flows: ≈20 and 200 ml/min

20 ml/min	H_2	C_2H_4
Vol.%	17.5	1.97
FE, %	≈27	≈27

200 ml/min	H_2	C_2H_4
Vol.%	37.6	2.75
FE, %	≈41	≈11

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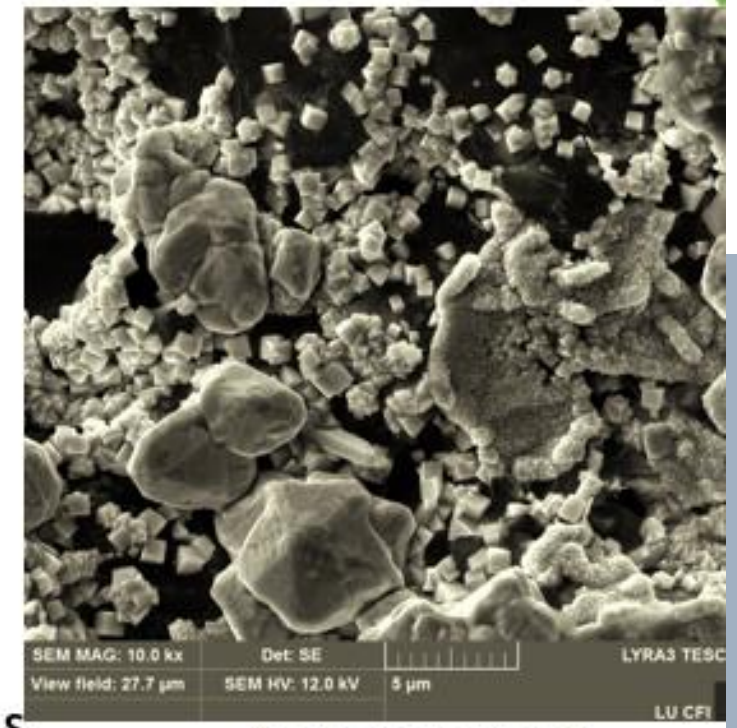
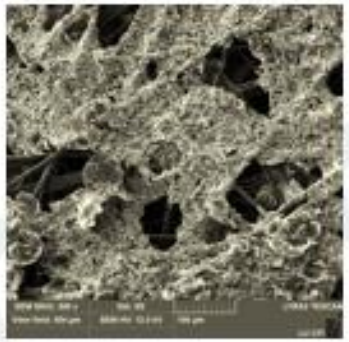
Summary of generated gas:

Current, mA	FE CH_4	FE C_2H_4	FE H_2
150	0.512%	0.140%	64.88%
200	0.273%	0.144%	65.21%

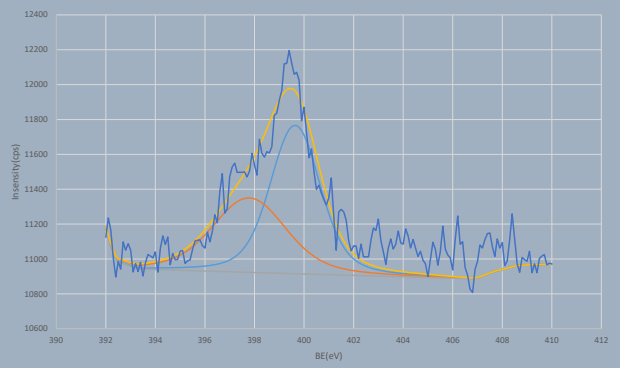




Summary:
SEM inspection of electrode after tests was performed. As it is seen from next pictures, GSS sheets are fully coated with copper. In some places GSS with copper falls off carbon paper, possible reason - GSS sheets are not tightly inserted in structure of carbon paper; deposition process could be improved.

Adhesion increase of copper catalyst on N-GSS

NaN_3 electrochemical exfoliation produces N-doped carbon nanoparticles. XPS verify the presence of C-N bond.



Electrode deposition at 150 mA for 2,5h , used $CuSO_4$, N-GSS solution, with N–GSS 5ml, 20ml Cu/N-GSS and HNO_3 – pH=2.7

Partial coverage/homogenity present. Reactivity, morphology, CO_2 reduction is specified.

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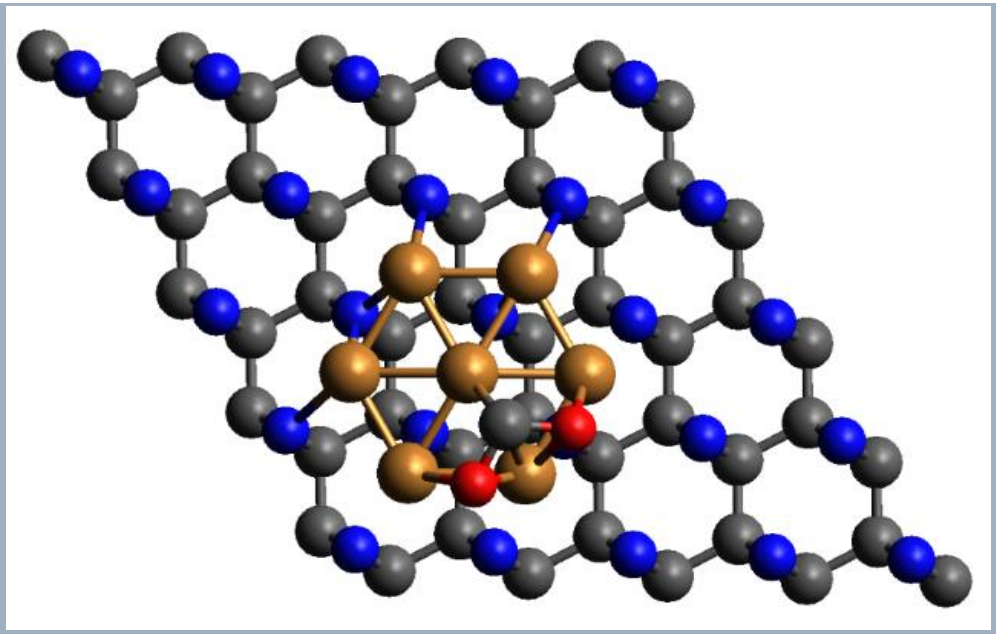
Adhesion increase of copper catalyst on GDE – ISSP

Selected results from large scale theoretical calculations of CO_2 reduction process on Cu/N-graphene suggested to chose nitrogenation of GDL:

Cu cluster is physisorbed and Cu-$C_{graphene}$ bond quite weak, bond population = 80 me (mili-electrons)

N atoms at graphene support allows for stronger chemisorption of Cu cluster, bond population of Cu-N = 303 me and N-$C_{graphene}$ = 344 me



Top view of CO_2 adsorbed on Cu nanocluster deposited atop N-saturated graphene monolayer

Adhesion increase of copper catalyst on GDE – ISSP

Summary

Selected results from large scale theoretical calculations of CO2 reduction process on Cu/N-graphene suggested to chose nitrogenation of GDL.
The adhesion of Cu films on C substrates can be improved by RF–N_2–plasma pre-treatment of the C substrate, what leads to a significant increase of the adhesion of the Cu coating by catalyzing an intermixing zone of Cu and C.

Hence, plasma treatment is a powerful tool to modify the interface in metal/carbon composites to achieve a better mechanical connection between two materials.

It is supported by literature: C.Schrank et al. Influence of thermal treatment on the adhesion of copper coatings on carbon substrates. Vacuum 80 (2005) 122–127:

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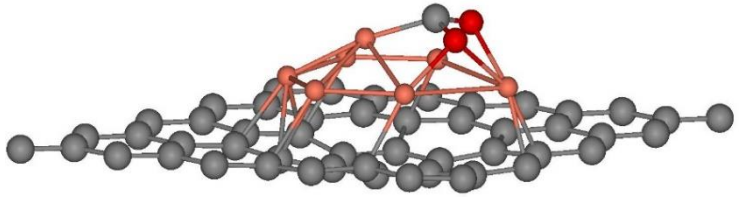
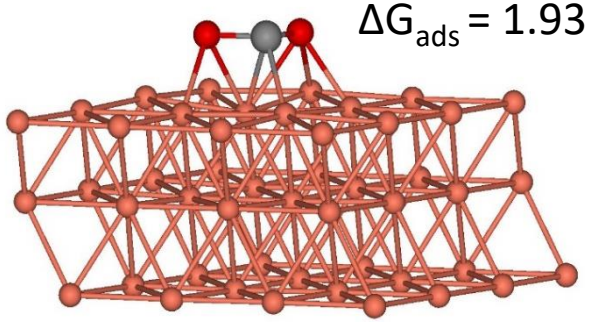
DFT: CO_2 adsorption on Cu_7@graphene nanostruture

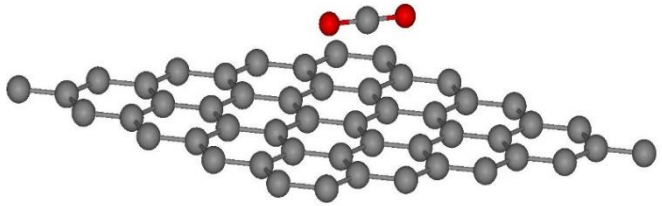
ΔG_{ads} = 1.55 eV



ΔG_{ads} = 1.93 eV



ΔG_{ads} = 2.42 eV



- CO_2 can be electrochemically reduced to hydrocarbons such as ethylene and methane via $2CO_2 + 12e^- + 8H_2O \rightarrow C_2H_4 + 12OH^-$ and $CO_2 + 8e^- + 6H_2O \rightarrow CH_4 + 8OH^-$
- CO_2 adsorption is the rate-determining step in CO_2 reduction reaction, and thus it is desirable to find/design catalyst sites that bonds CO_2 stronger than H adsorption (ΔG_{ads} = 2.93 eV)
- The stronger binding of CO_2 to the Cu_7 nanocluster we explain by the presence of wide <111> grain boundaries region on the Cu_7 nanocluster with respect to Cu (111) surface. Experimentally measured enhancement in Faraday efficiency of generating multi-carbon hydrocarbons is correlated with the density of the Cu catalyst grain boundary areas*. The adsorption properties of neighboring Cu sites are significantly perturbed by the presence of nearest C, and the stronger Cu-O bonding is formed on the catalyst surface, which also can enhance $H_2C{=}CH_2$ evolution. * X. Feng, K. Jiang, S. Fan and M. W. Kanan, ACS Cent. Sci., 2016, 2, 169–174.

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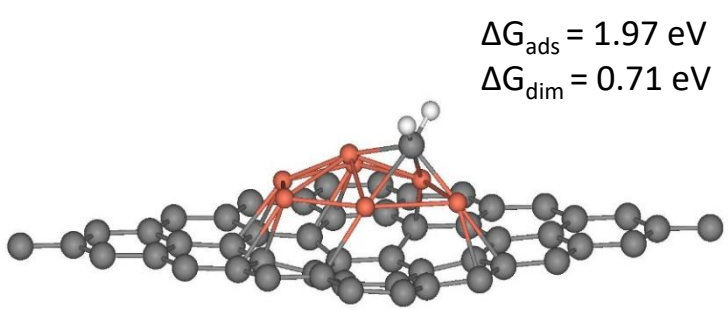
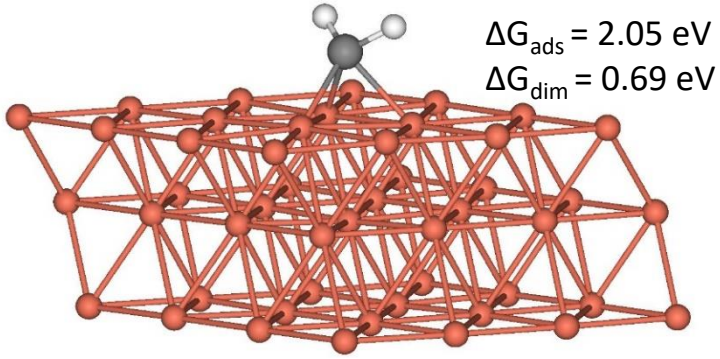
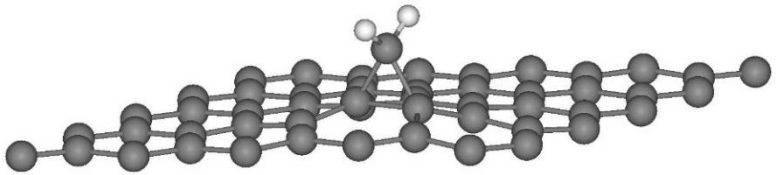
DFT: CH_2 dimerization on Cu_7@graphene nanostruture







- The most probable pathways for C_2H_4 formation is that one that shares an intermediate with the pathway to CH_4.
- The $*CH_2$ dimerization is a crucial step for the final C_2H_4 production (“carbene” mechanism).
- The lowest dimerization barrier is predicted for the pristine graphene due do lowest free adsorption energy

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DFT: Conclusions

- Cu cluster at graphene reproduce the facets of the most stable Cu(111) surface. In agreement with recent experimental observations, we predict the stronger binding of CO_2 to the Cu_7 nanocluster due the presence of wide <111> grain boundaries region on the Cu_7 nanocluster with respect to Cu (111) surface. Based on this we predict the larger is the length of grain boundaries of the Cu_n nanocluster deposited at graphene the more selective to the C_2H_4 could be the catalyst
- The lowest dimerization barrier is predicted for the pristine graphene due do lowest free adsorption energy, meaning that the whole CO_2 reduction reaction taking place at the grain boundary of Cu_n@graphene nanocluster may lead to improved selectivity to ethylene.

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Thank You for attention!

Further Information:

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