After the RISEnergy Transnational Access, Users are required to submit a User Report. This should be done within 4 weeks after the Access is completed unless otherwise agreed. The User Report will be given to the User(s) by the WP2 leader. The report contains sections related to the work performed, the main results and observations that were achieved.

This document should be completed, signed, and sent by e-mail to risenergy@for.kit.edu.

Summary questionnaire for Users who have been granted Transnational Access (TA) under the RISEnergy project Horizon Europe TA scheme. More information on RISEnergy TA can be found in "General Rules" and in "Access Policy" which can be found on the RISEnergy webpage.

Please complete, sign, and send this form, together with the Cost claim by e-mail to risenergy@for.kit.edu with title: RISEnergy APPXXX - reports.

General information about the project	
Project title (as used in Application)	CO_2 to Chemicals by Renewable Assisted Electrochemical Reduction
Project number (APPXXX) and acronym (max 15 characters)	170 - CtoCHEM
RISEnergy RI(s) accessed	TA74 – FZJ-LLEC
Keywords (up to five, free text)	Electrolysis; CO2 reduction; Hydrogen
Arrival date (in town where RI is located)	17.10.2025
Departure date (from town where RI is located)	14.01.2026
Starting date of Access (first day at RI)	20.10.2025
Finishing date of Access (last day at RI)	13.01.2026
Number of days not using the RI (during the above period)	5
Reason for not using RI those days (describe)	Christmas Holiday
Number of days using the RI	90
Number of Users granted Access (group size)	1
Comments	

User
User group leader or sole applicant (user group member 1)

First name	
Last name	
Affiliation / Employer	
Country of Employer	
E-mail	
User travelling to RI?	
Comments	
User group member 2	
First name	
Last name	
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User travelling to RI?	
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Please insert more fields if your groups had more than four members.	
Access Summary Report - work performed and initial results	
Brief description of the objectives of your project (up to 200 words)	

Electrocatalytic CO_2 reduction (ECR) is a promising strategy for mitigating carbon emissions while converting CO_2 into value-added chemicals. Achieving high efficiency and selectivity in ECR requires careful optimization of several factors, including catalyst surface properties, morphology, electrochemical activity, electrolyte composition, pH, and electrochemical cell design. Controlling reaction pathways to favor multi-carbon (C_2^+) products remains a central challenge.

Tandem electrode architectures have emerged as an effective approach to address this challenge by spatially separating reaction steps. In such systems, a first catalyst layer selectively converts CO_2 to CO, which is subsequently further reduced on a second catalyst layer, typically copper, to form hydrocarbons and oxygenates. This strategy enables enhanced local CO availability, improved C-C coupling, and increased selectivity toward C_2 products such as ethylene and ethanol.

In ECR, electrical energy drives the activation of CO_2 and water molecules, enabling the formation of various single carbon (C_1) products depending on the number of electrons transferred. Beyond C_1 products, efficient C-C coupling is essential for generating higher-value chemicals. Metal phthalocyanines, such as cobalt phthalocyanine (CoPc), are attractive CO generating catalysts due to their stability, tunability, and high selectivity, making them particularly suitable for tandem ECR systems.

Activities performed (up to 600 words)

The project was designed to be completed within a three-month timeframe. Following the selection of CoPc as the primary catalyst, electrode preparation was initiated immediately. CoPc is a well-established catalyst for the electrochemical reduction of CO_2 to CO, exhibiting high Faradaic efficiency (FE). Accordingly, CoPc based electrodes with two different loading ratios were prepared using RI's spray coater (Sonotek ExactaCoat). Catalyst inks were prepared with CoPc to carbon black (CB) mass ratios of 1:4 and 1:10. In these formulations, CB served as a conductive support; for example, 4 mg of CB was used per 1 mg of CoPc in the 1:4 formulation. Nafion was used as a binder in all ink compositions. The inks were spray-coated onto carbon paper to fabricate the working electrodes.

Each electrode with a different loading ratio was tested individually in an ElectroCell flow cell. Electrochemical measurements were performed using an Autolab potentiostat/galvanostat controlled by NOVA software. The testing protocol began with cyclic voltammetry (10 cycles) for electrode activation, followed by galvanostatic measurements at current densities ranging from 10 to 200 mA. Gas chromatography (GC) analysis was conducted at each current step to identify and quantify gaseous products, and Faradaic efficiencies for CO were calculated accordingly.

Based on these results, sputtered copper electrodes were prepared using the 1:10 CoPc formulation, which showed the highest CO FE, to fabricate tandem electrodes. Copper sputtering was performed using a Quorum sputtering device, targeting loadings of 0.4 mg/cm^2 and 0.8 mg/cm^2. For comparison, sputtered silver electrodes with loadings of 0.2 mg/cm^2 and 0.4 mg/cm^2 were also prepared.

To investigate the influence of ionomer content, sputtered copper electrodes were divided into four groups for each loading and labeled G0, G1, G2, and G3, corresponding to 0, 30, 60, and 90 µL of Nafion ionomer drop-cast onto the electrode surface, respectively. In addition, higher-loading sputtered copper electrodes were prepared and further labeled according to ionomer content as G8-0, G8-1, G8-2, and G8-3. All electrodes were subsequently tested electrochemically in a flow cell, and gaseous products were analyzed by GC. The same experimental methodology was applied to sputtered silver electrodes.

For further investigation, three tandem electrode configurations were selected. Final tandem electrodes were fabricated using sputtered copper combined with CoPc. In addition, tandem electrodes based on sputtered silver and silver nanoparticles were prepared. For all tandem electrodes, the G1 condition (30 µL Nafion) was applied by spray coating onto the sputtered substrates, followed by CoPc drop-casting, silver sputtering, or silver nanoparticle drop-casting to complete the tandem architectures. The resulting electrodes were labeled CuSp-CoPc1, CuSp-CoPc2, CuSp-AgSp1, CuSp-AgSp2, CuSp-AgNP1, and CuSp-AgNP2, where "1" and "2" correspond to metal loadings of 0.4 mg/cm² and 0.8 mg/cm², respectively.

Furthermore, the effect of different ionomers was investigated by drop-casting Sustainion, Orion, and Piperion onto sputtered copper electrodes. An ionomer loading of 30 µL was applied for each ionomer, as this amount was identified as the optimal loading based on Nafion experiments and was therefore used for direct comparison. The electrodes were labeled Naf1, Naf2, Or1, Or2, Pip1, Pip2, Sus1, and Sus2, corresponding to Nafion, Orion, Piperion, and Sustainion, respectively. The numbers 1 and 2 denote copper loadings of 0.4 mg/cm² and 0.8 mg/cm². All electrodes were tested under identical flow-cell conditions.

Overall, this systematic study resulted in the successful fabrication, electrochemical evaluation, and gas chromatographic analysis of more than 30 distinct electrode configurations, representing a comprehensive exploration of catalyst loading, ionomer chemistry, and tandem electrode design for ECR.

Scientific results (up to 800 words)

Initial results demonstrated that CoPc is an effective catalyst for CO_2 to CO conversion. CoPc electrodes with a 1:4 CoPc to carbon black (CB) ratio exhibited stable performance, with an average CO Faradaic efficiency (FE) of approximately 40% (Figure 1A). In contrast, the 1:10 ratio showed significantly higher CO Faradaic efficiencies at low current densities, reaching up to 90% in the 10–80 mA range (Figure 1B). Although the efficiency gradually decreased at higher current densities, it remained superior to that of the 1:4 electrode across the entire current range. The lower CoPc loading resulted in improved catalyst dispersion and increased accessibility of Co–N_4 active sites. This behavior is consistent with literature reports, which associate higher metal phthalocyanine loadings with aggregation effects that limit active site utilization and reduce catalytic efficiency.

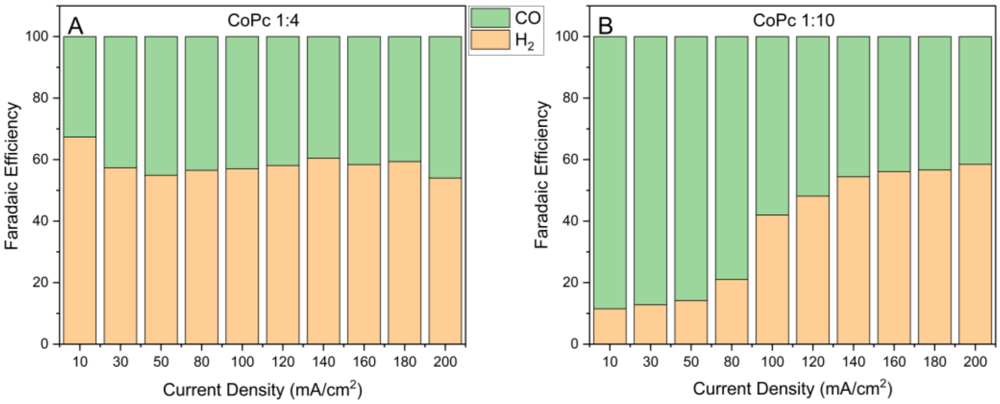

Figure 1: Faradaic efficiency plots for CB supported CoPc with 1:4 (A) and 1:10 (B) ratios.

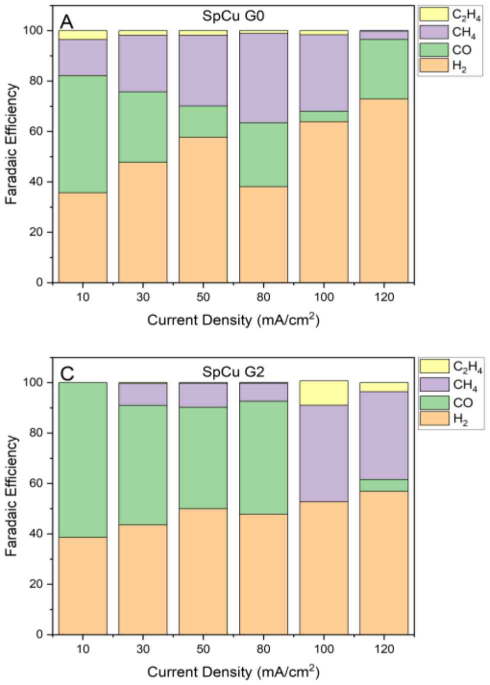

Figure 2: Faradaic efficiency of sputter copper electrodes in 0,4 mg/cm^{-2}

Systematic flow-cell testing revealed that ionomer content strongly influences electrochemical performance, with a moderate Nafion loading (30 µL, G1) providing the most favorable balance between activity, stability, and selectivity. This trend remained consistent even at higher sputtered copper loadings, as shown in Figure 3B. A key outcome of the study was the systematic evaluation of sputtered copper electrodes on carbon paper. Copper electrodes with different sputtering loadings exhibited distinct product selectivities, resulting in markedly different FE’s toward methane and ethylene. Higher methane FE’s were observed at increased copper loadings, as illustrated in Figure

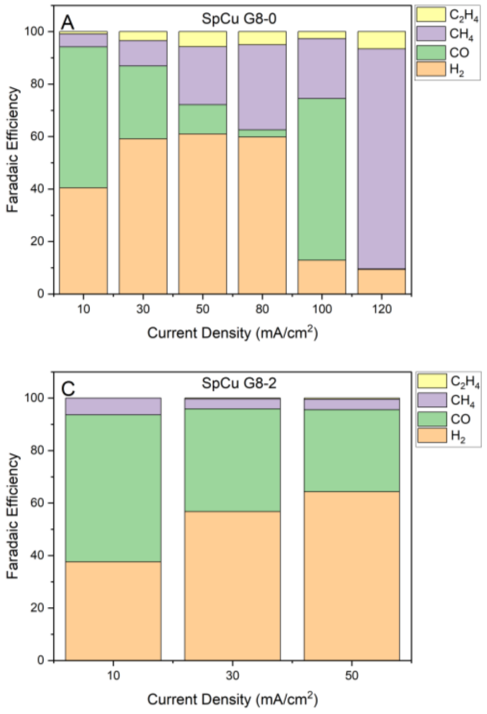

Figure 3: Faradaic efficiency of sputter copper electrodes in 0,8 mg cm^{-2}

3. Among the tested conditions, a copper loading of 0.4 mg/cm² demonstrated superior overall performance, achieving ethylene FE's of approximately 20%.

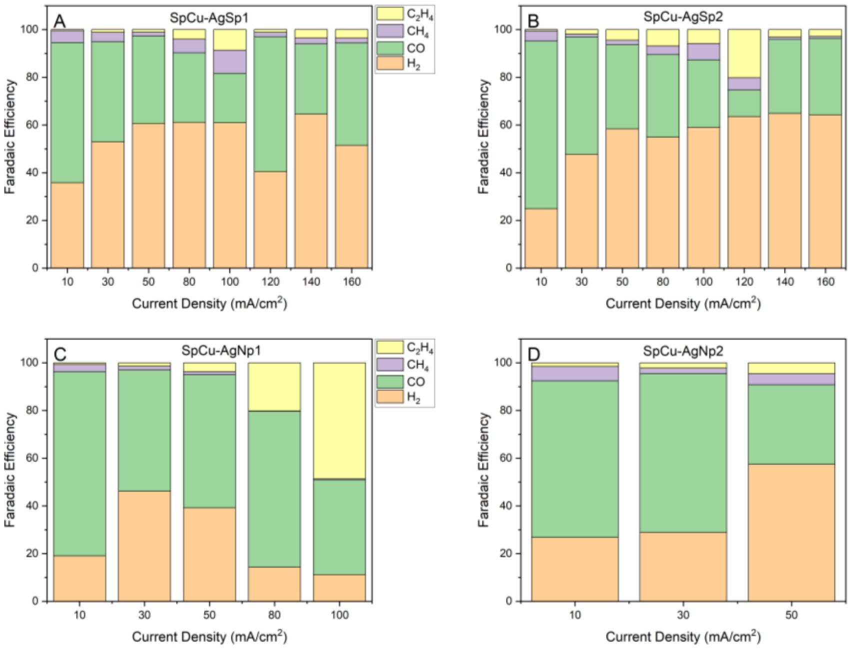

Figure 4: Faradaic efficiency of Silver based tandem electrodes.

The electrochemical results revealed clear loading-dependent selectivity trends. CuSp-CoPc1, incorporating a lower sputtered copper loading, favored ethylene formation, achieving FE's of approximately 40% at current densities of 50 and 80 mA (Figure 5A). In contrast, the higher copper loading configuration, CuSp-CoPc2, exhibited a pronounced shift toward methane production, with FE's exceeding 50% (Figure 5B). These results highlight the critical role of copper loading in governing product selectivity and in selecting appropriate catalyst configurations to achieve targeted product distributions in tandem electrode architectures.

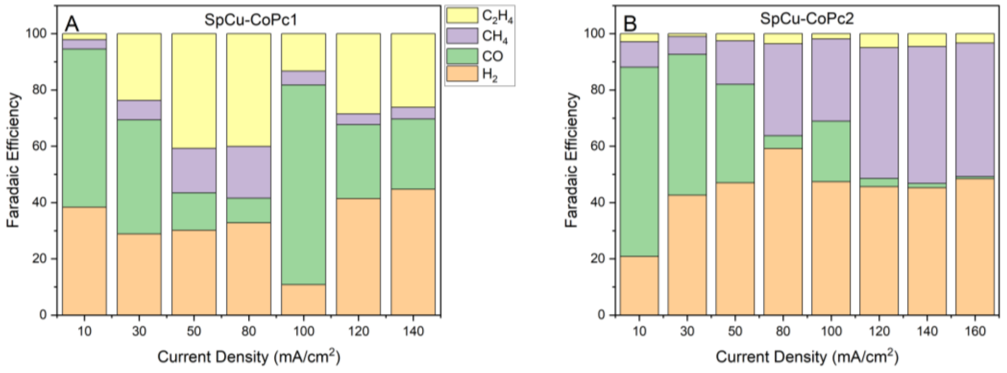

Figure 5: Faradaic efficiency of CoPc tandem electrodes with different loading of sputter copper

In comparison, tandem electrodes based on sputtered silver did not achieve acceptable Faradaic efficiencies for ethylene formation (Figure 4A-B). This behavior is likely associated with restricted gas diffusion and partial blockage of active copper sites caused by the dense morphology resulting from dual sputtering. In contrast, tandem electrodes incorporating silver nanoparticles exhibited acceptable ethylene FE (Figure 4C),

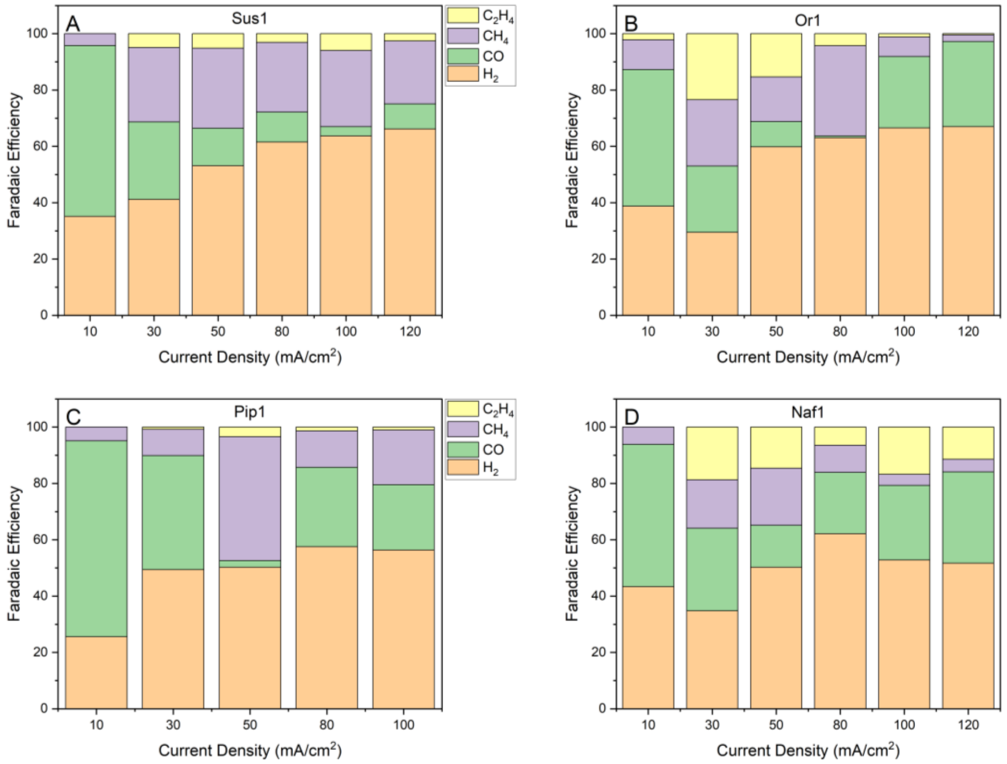

Figure 6: Faradaic efficiency of sputter copper electrodes in 0,4 mg cm^{-2}

suggesting that the more porous nanoparticle layer preserves gas diffusion pathways and enables effective C–C coupling.

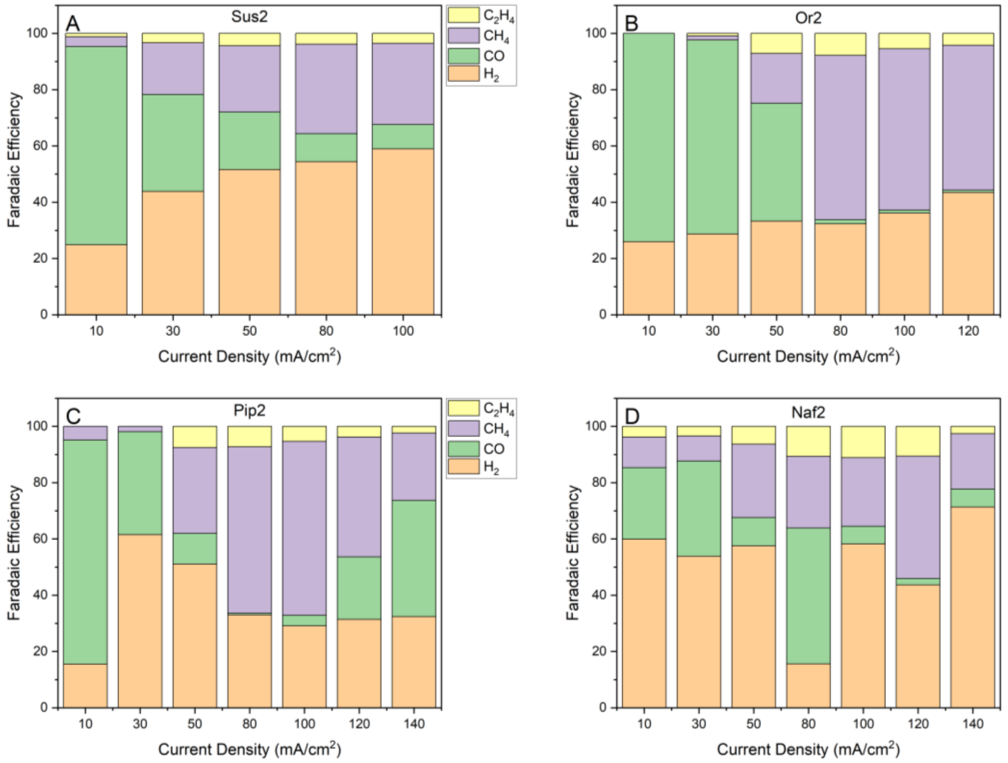

Figure 7: Faradaic efficiency of sputter copper electrodes in 0,8 mg cm^{-2}

The influence of ionomer chemistry was investigated using Nafion, Sustainion, Orion, and Piperion on sputtered copper electrodes with two different copper loadings, both in tandem electrode configurations and ionomer-loading studies. Piperion significantly shifted product selectivity toward methane formation (Figure 6C). At higher copper loading, methane-selective behavior was observed for all tested ionomers (Figure 7), indicating a strong combined effect of copper loading and ionomer chemistry. Notably, the highest methane Faradaic efficiencies were obtained with Piperion at the higher copper loading (Figure 7C).

Orion promoted C_2 product formation, with ethylene FE exceeding 20% at 30 mA on 0.4 mg/cm² sputtered copper electrodes, similar to the behavior observed with Nafion, while also exhibiting methane Faradaic efficiencies of at least 40%. In contrast, Sustainion did not significantly affect the product selectivity of the prepared electrodes.

Overall, the study established clear structure performance relationships among catalyst loading, ionomer chemistry, and tandem electrode design, providing a strong foundation for future optimization and mechanistic studies of CO_2 electroreduction systems

Due to the limited project timeframe, Nafion was selected as the ionomer for tandem electrode fabrication to ensure experimental consistency and timely completion. Nevertheless, the observed ionomer dependent trends suggest that further investigations using alternative ionomers can be pursued in the home laboratory beyond RI.

Interpretation of the results (up to 400 words)

The observed trends in activity and product selectivity can be explained by the combined effects of catalyst loading, ionomer content, and tandem electrode architecture on the local reaction environment during CO_2 electroreduction. For CoPc-based electrodes, the higher CO Faradaic efficiency obtained with the 1:10 CoPc-to-carbon black ratio is attributed to improved dispersion of CoPc molecules and enhanced accessibility of active $Co{-}N_4$ sites, which facilitates efficient CO formation and electron transfer.

For sputtered copper electrodes, product selectivity was strongly dependent on copper loading. Lower copper loadings favored ethylene formation, suggesting that moderate surface *CO coverage and optimal binding strength promote C–C coupling. In contrast, higher copper loadings shifted selectivity toward methane, which can be associated with increased hydrogenation activity and suppressed C–C coupling under conditions of higher local proton availability.

Ionomer content played a critical role in regulating ionic transport, wettability, and gas diffusion at the catalyst interface. Moderate Nafion loading (30 μL) provided the most favorable balance between electrochemical activity and mass transport, while excessive ionomer coverage likely hindered CO diffusion or partially blocked active sites. Differences observed among Nafion, Sustainion, Orion, and Piperion further indicate that ionomer chemistry significantly influences the local pH and reaction microenvironment.

Finally, tandem electrode architectures enhanced C_2 product formation by coupling efficient CO generation with subsequent reduction on copper, highlighting the importance of spatially integrated catalyst design for improved CO_2 electroreduction performance.

Main achievements during the TA related work (up to 250 words)

During the TA related work, significant progress was achieved in the systematic design, fabrication, and evaluation of electrocatalysts and tandem electrode architectures for electrochemical CO_2 reduction. A major achievement of this project was the successful preparation and optimization of CoPc based electrodes, where the influence of catalyst loading on CO FE and operational stability was clearly established. The CoPc 1:10 catalyst to CB ratio was identified as the optimal configuration, exhibiting CO FE's of up to 90% at low to moderate current densities.

Another key accomplishment was the controlled fabrication of sputtered copper and silver electrodes with precisely defined metal loadings. By systematically varying copper loading and ionomer content, clear structure selectivity relationships were revealed, demonstrating that lower copper loadings favor ethylene formation, while higher loadings shift selectivity toward methane. The critical role of ionomer chemistry was further demonstrated through comparative studies using Nafion, Sustainion, Orion, and Piperion, highlighting the ability of ionomers to tune the local reaction environment and product distribution.

The project also successfully demonstrated the feasibility of tandem electrode architectures by integrating CoPc, sputtered copper, sputtered silver, and silver nanoparticles. Several tandem configurations achieved enhanced C_2 product formation, with ethylene FE's reaching approximately 40%. In total, more than 30 distinct electrode configurations were fabricated, tested in flow-cell systems, and analyzed using in situ GC.

Overall, this work established robust experimental methodologies, generated valuable mechanistic insights into catalyst ionomer loading interactions, and provided a strong foundation for future optimization of ECR systems.

Data Management

Project data are maintained by Kadir Türkmen and Dr. Ilias Stamatelos. The project data include gas chromatography results, Faradaic efficiency calculations, and electrochemical test results obtained under galvanostatic conditions.

Difficulties during the TA related work (up to 250 words)

[List problems and issues, you had, completing out your research project: Did you get access to all the necessary equipment, facilities, databases, etc.?
If not, please specify the problems that occurred and list equipment the was not working or accessible.]

Intended publications

At present, no publication has resulted from this work; however, further experimentation may lead to future publications. Additional catalyst syntheses are planned, and the outcomes of this project are expected to serve as a fundamental basis for these studies. The data generated in this study were primarily intended for use in the author's master's thesis, as the project was initiated for this purpose prior to the collaboration.

Expected impact

Future collaboration between host and user institutes are planned submitting proposals.

Conclusions / additional comments

The characterization section of the report is currently missing. RI will provide later the characterization data, including SEM/EDX, TEM, and XPS analyses.

Did you complete the European Commission User questionnaire https://ec.europa.eu/eusurvey/runner/RIsurveyUSERS?

☒ *Yes* ☐ *No*

Feedback – HSE, Ethics and Satisfaction

Please rate on a scale from 1 (excellent) to 5 (poor). Feel free to provide additional comments					
Practical information on how to apply for Transnational Access and the overall application process	1 (excellent)	2	3 (neutral)	4	5 (poor)
	☒	☐	☐	☐	☐
Comment					
Information provided, once your project was accepted, on how to proceed	1 (excellent)	2	3 (neutral)	4	5 (poor)
	☒	☐	☐	☐	☐
Comment					
Support received at the site(s) regarding technical/scientific matters and logistics	Have you got sufficient support from the RI staff during the project? If not, please, specify the problems. ☒ *Yes* ☐ *No*				
Please specify any problems					
RI extension / upgrades required	In your opinion, is the RI needed to be upgraded? If yes, please give an explanation. ☐ *Yes* ☒ *No*				
Please specify					
Problems with local regulations	Have you had any problems with regulations of the visited RI owner (HSE, lab working hours, etc.)? If yes, please, specify ☐ *Yes* ☒ *No*				
Please specify					
Health and safety issues	Did you encounter any health or safety issue during your research? Please provide details. ☐ *Yes* ☒ *No*				
Please provide details					
Environment & Ethics	Did your research involve the use of elements that may cause harm to the environment, to animals or plants? Please provide details. ☐ *Yes* ☒ *No*				
Please provide details					
Environment & Ethics	Did your research deal with endangered fauna and/or flora and/or protected areas? Please provide details. ☐ *Yes* ☒ *No*				

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<tr><td>Environment & Ethics – Dual use</td><td>Does your research have the potential for military applications? Please provide details.
☐ Yes ☒ No</td></tr>
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<tr><td>Environment & Ethics – Misuse</td><td>Does your research have the potential for malevolent /criminal/terrorist abuse? Please provide details.
☐ Yes ☒ No</td></tr>
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<tr><td>Environmental issues</td><td>Were any potentially dangerous substances (materials / gases etc.) released into the environment (atmosphere, water, or land)? Please provide details.
☐ Yes ☒ No</td></tr>
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<tr><td>Ethics issues</td><td>Are there any other ethics issues that should be taken into consideration? Please specify
☐ Yes ☒ No</td></tr>
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<tr><td>Overall impression of communication and interaction after finishing your TA and related work</td><td><table>
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<tr><td colspan="2">Suggestions for facilities not included in RISEnergy which you would use for your research</td></tr>
<tr><td colspan="2">[Please provide suggestions for specific type of facilities missing (RI gaps) or measurement / experiments you would like to perform which cannot be done on current RISEnergy facilities.]</td></tr>
<tr><td colspan="2">Suggestions how RISEnergy can improve future TA programme, how to make the TA more impactful and how to enable the achievement of high TRL levels</td></tr>
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[Your suggestions]

Feedback – Pro-active Innovation Support

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<tr><td>Awareness</td><td>Did you know about the pro-active innovation support of RISEnergy?
☐ Yes ☒ No</td></tr>
<tr><td colspan="2"><i>[Please specify how you learned about the pro-active innovation support]</i></td></tr>
<tr><td>Personal experience</td><td>Have you taken advantage of or benefited from the pro-active innovation support?
☐ Yes ☒ No</td></tr>
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<tr><td>Information/service provided by the pro-active innovation support?</td><td><table><tr><td>1 (excellent)</td><td>2</td><td>3 (neutral)</td><td>4</td><td>5 (poor)</td></tr><tr><td>☐</td><td>☐</td><td>☒</td><td>☐</td><td>☐</td></tr></table></td></tr>
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I declare that the above provided information and especially that information on the number of days visited the RI is correct.

☒ *I have read the RISEnergy privacy policy for participation in the RISEnergy TA and consent to participation and the associated data processing.*

Your full name:

Your signature: