Supplementary Information (SI) for RSC Sustainability.

Supporting Information

The Best of Both Worlds: Stacked Catalytic Layers for the Electrocatalytic Generation of CO in Zero-Gap Electrolyzers

Lucas Hoof[a]†, Kevinjeorjios Pellumbi[a]†, Didem Cansu Güney[b], Dennis Blaudszun[a], Franz Bommas[a], Kai junge Puring[a], Daniel Siegmund[a,c], Rui Cao[d], Katharina Weber[b]* and Ulf-Peter Apfel[a,d]*

a. Fraunhofer Institute for Environmental, Safety and Energy Technology, UMSICHT, Oberhausen, Germany. E-mail: ulf-peter.apfel@umsicht.fraunhofer.de

b. Aalen University, Research Institute for Innovative Surfaces FINO, Aalen, Germany. E-mail: katharina.weber@hs-aalen.de

c. Inorganic Chemistry, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Bochum, Germany. E-mail: ulf.apfel@rub.de

d. Key Laboratory of Applied Surface and Colloid Chemistry, Shaanxi Normal University, Xi'an, China. E-mail: ruicao@snnu.edu.cn

† These authors contributed equally

Preparation of the gas diffusion Electrodes and different catalyst layers

For all cathode inks, 500 mg of Ag-NPs (Alfa Aesar, 20–40 nm) and a varying amount of the used binder, based on the catalyst mass, were dissolved in 30 g of a 3:1 isopropanol/water mixture.

In the case of the PiperION-ink, the A5-Piperion-Ionomer (Versogen) were used. After 15 min in an ultrasonic bath, a dispersion tool (IKA Ultra-TurraxT18D) was used for 90 s at 13,400 rpm to homogenize the ink. The cathode ink was then sprayed onto a 365-µm-thick carbon cloth (W1S1010, Fuel Cell Store) until a total silver loading of 2.5 mg cm^{-2} was achieved.

PTFE-based GDEs were prepared in a similar fashion. For the preparation of the PTFE-inks a 60 wt.% dispersion (Quintech) was employed. To better stabilize the PTFE-suspension, in each PTFE ink 100 mg of Triton X-100 (Thermofischer) were added as a surfactant. After ultrasonication and homogenation with a dispersion tool, the PTFE dispersion was added following by 15 min of ultrasonication. Prior to electrochemical testing, all PTFE-bound GDEs were annealed at 300°C to remove any surfactants.[1]

The cathodes were cut with a punching iron of 16 mm diameter directly resulting in an active area of 2 cm^2.

Contact angles measurements were performed with the help of a VHX1000 digital microscope. 2 µL of the H_2O were placed by hand on the surface of the GDE surface, with contact angles being recorded after 30 seconds of relaxation. The average of ten drops for each solvent was taken.

Electrochemical investigation

Electrochemical investigation were performed at our previously developped set-up. [2] The cell was place in an oven together with the 0.1 $KHCO_3$ anolyte at 60°C and allowed to condition. For the detection of changes in the volume of the gas flow due to CO_2 crossover through the AEM and gas-forming reactions an Argon flow of 5.5 mL min^{-1} (10 vol.%) was added as an internal standard to the 50 mL min^{-1} CO_2 flow (λCO_2: 12). Both inlet gases were controlled by mass flow controllers (Bronkhorst). For the humidification of the inlet gas stream, a bubbler filled with MilliQ water (18.2 MΩ · cm) was put into a temperature-controlled water bath at 55 °C outside of the oven. A slight overpressure of 100 mbar(g) was applied on the cathode side through the help of a back-pressure controller (Specken & Drumag). The anode circuit flow was controlled by a peristaltic pump at 20 mL min^{-1} using 0.1 M $KHCO_3$ as the anolyte. For all experiments, the cell was operated with the anode facing upwards and the cathode facing downwards. The cathode and anode substrate flows were directed through the cell in a counterflow arrangement meaning that the directions of the gas inlet flow and the anolyte flow are opposite to each other. All experiments were performed at least twice using a Gamry 3000 Potentiostat/Galvanostat. The electrocatalytic activity and selectivity were determined by performing chronopotentiometry (CP) measurements at a current density of −300 mA cm^{-2} for at least 3 h. Galvanostatic electrochemical impedance spectra were obtained in a 2-electrode setup at 300 mA cm^{-2}. Electrochemical impedance spectra were recorded between 1 Hz-100 kHz with 10 mA RMS perturbation. The consistency of the EIS data was confirmed by performing the Kramers–Kronig test.

Rheology

The rheological tests on catalyst inks were carried out using a rotating rheometer equipped with a cone-plate system. The cone had a diameter of 75 mm and an angle of 1° to ensure controlled shear rates. Prior to the measurements, all ink samples were subjected to a 15-minute treatment in an ultrasonic bath at 20 °C, followed by a 90 second dispersion at 13,500 rpm with an IKA ULTRA-TURRAX. The catalyst inks were then analysed at a deformation amplitude of 1 % within the linear viscoelastic range. The measurements covered a frequency range from 100 Hz to 0.1 Hz at temperatures of 25 °C, 50 °C and 70 °C.

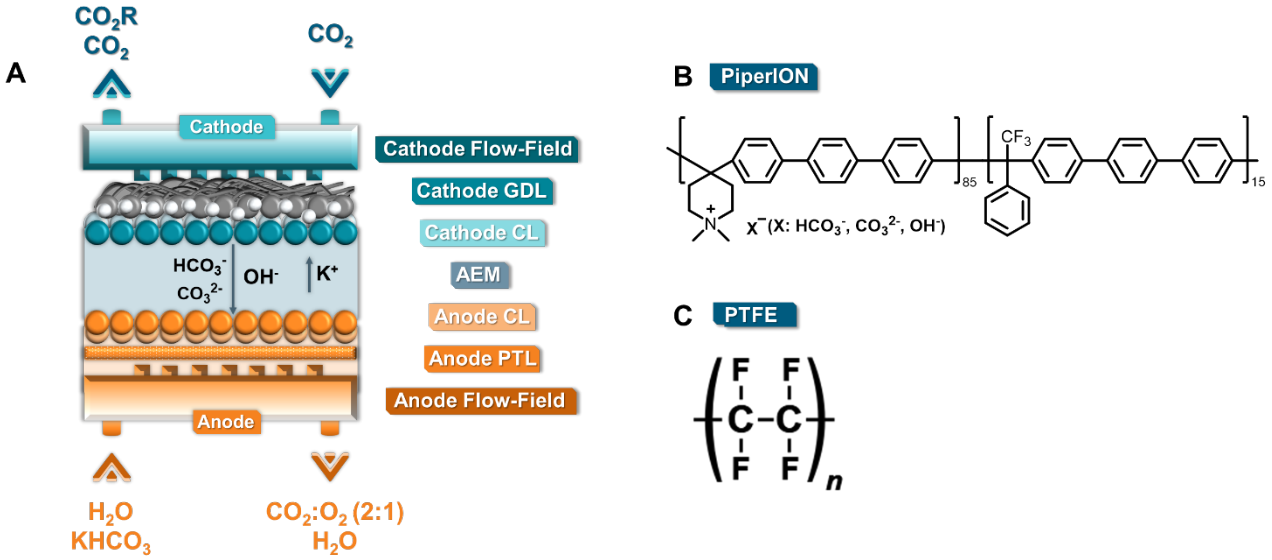

Figure S1: Schematic representation of an AEM-based ZGE as well as of the structures of the two herein employed binders, PTFE and PiperION.

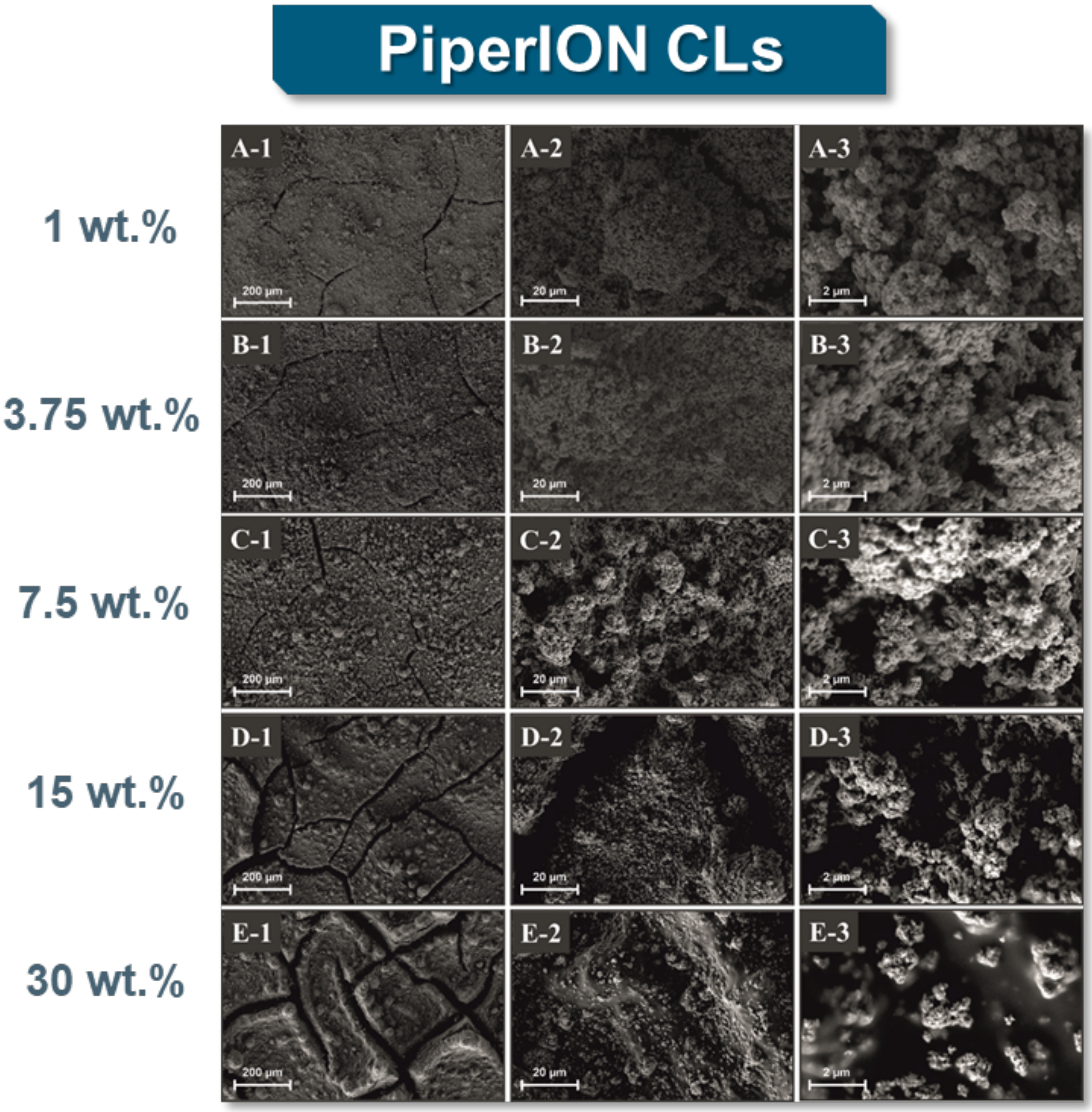

Figure S2: Top view SEM analysis of the PiperION-CLs at different binder contents at a magnification of x50, x500, x5000 from left to right.

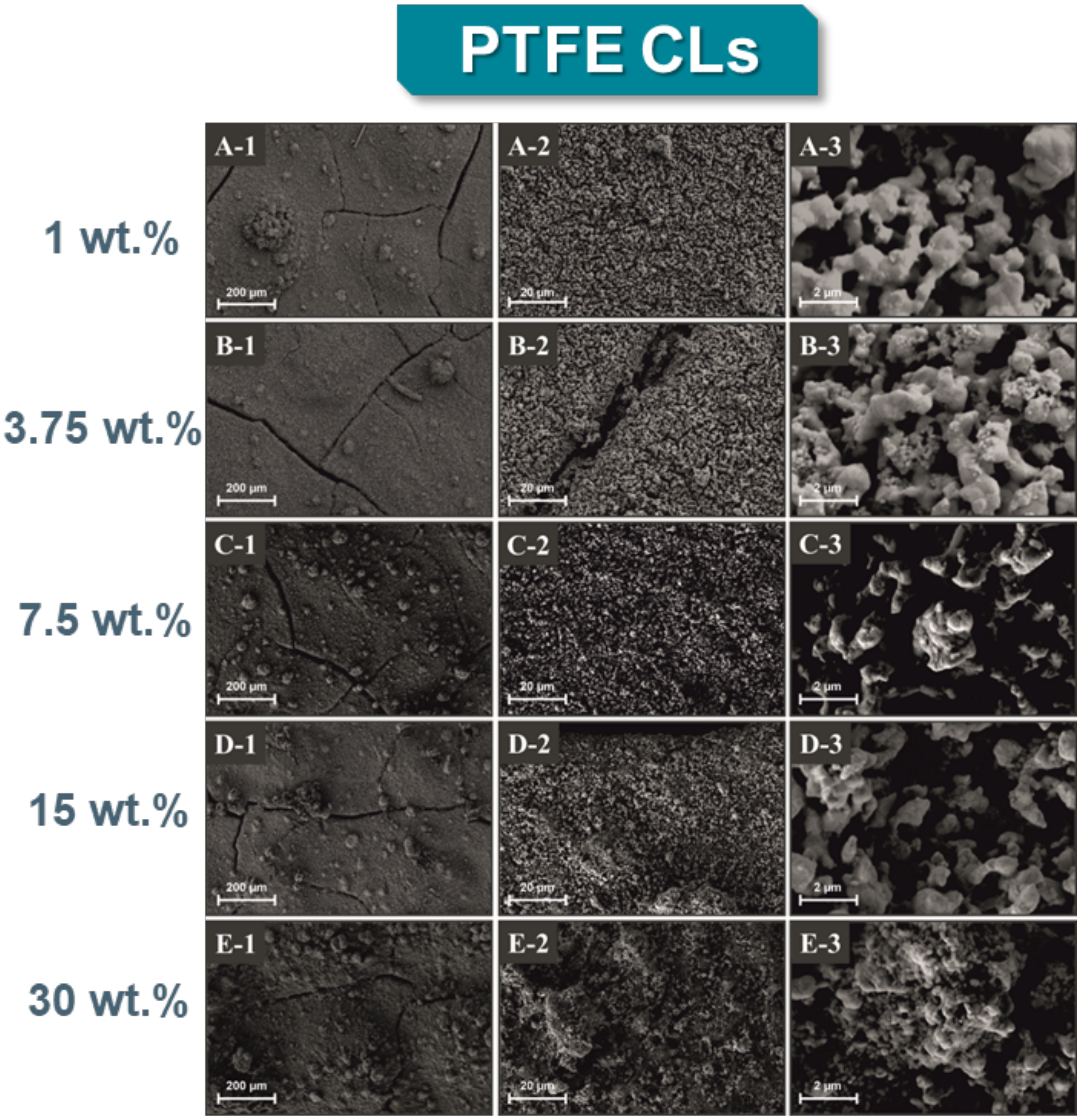

Figure S3*:* Top view SEM analysis of the PTFE-CLs at different binder contents at a magnification of x50, x500, x5000 from left to right.

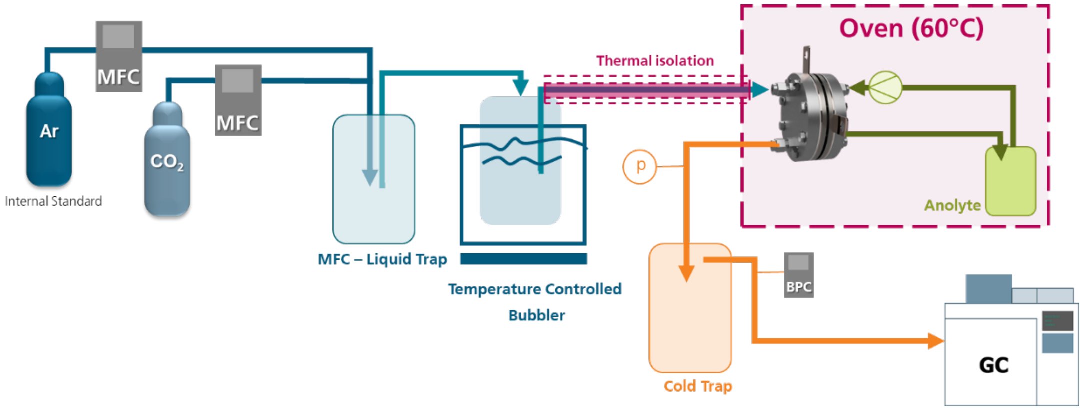

Figure S4: Schematic representation of the CO_2 electrolysis set-up employed in this work.

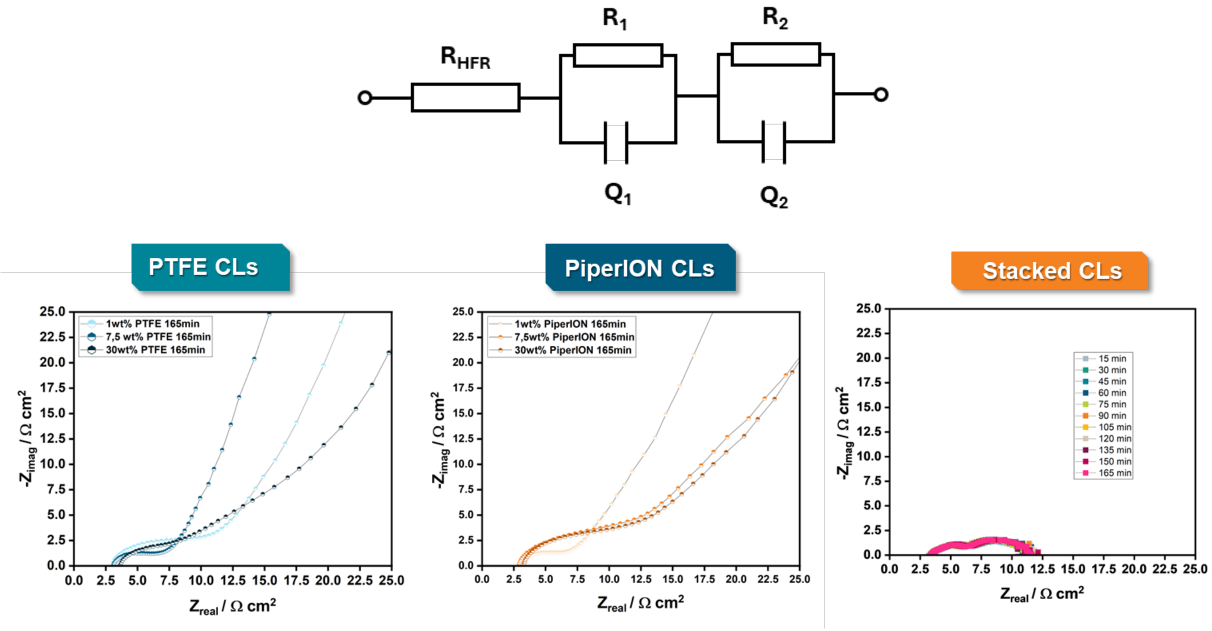

Figure S5: Nyquist plots of the galvanostatic impedance spectroscopy performed at 300 mA cm^{-2}, as well as the model circuit for the two-electrode system employed. For the PiperION and PTFE-CL the impedanc spectra at 165 min are shown for reasons of clarity.

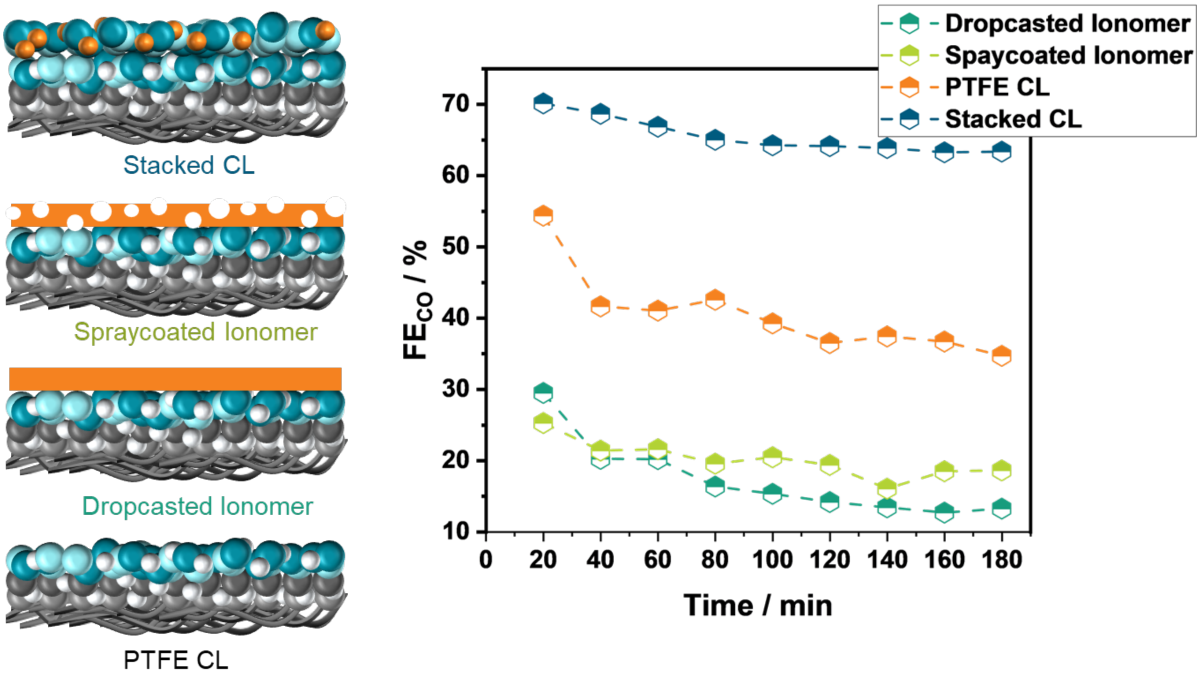

Figure S6: Control experiments showing the influence of Ag in the PiperION catalytic layer of the stacked CL at 300 mA cm^{-2}.

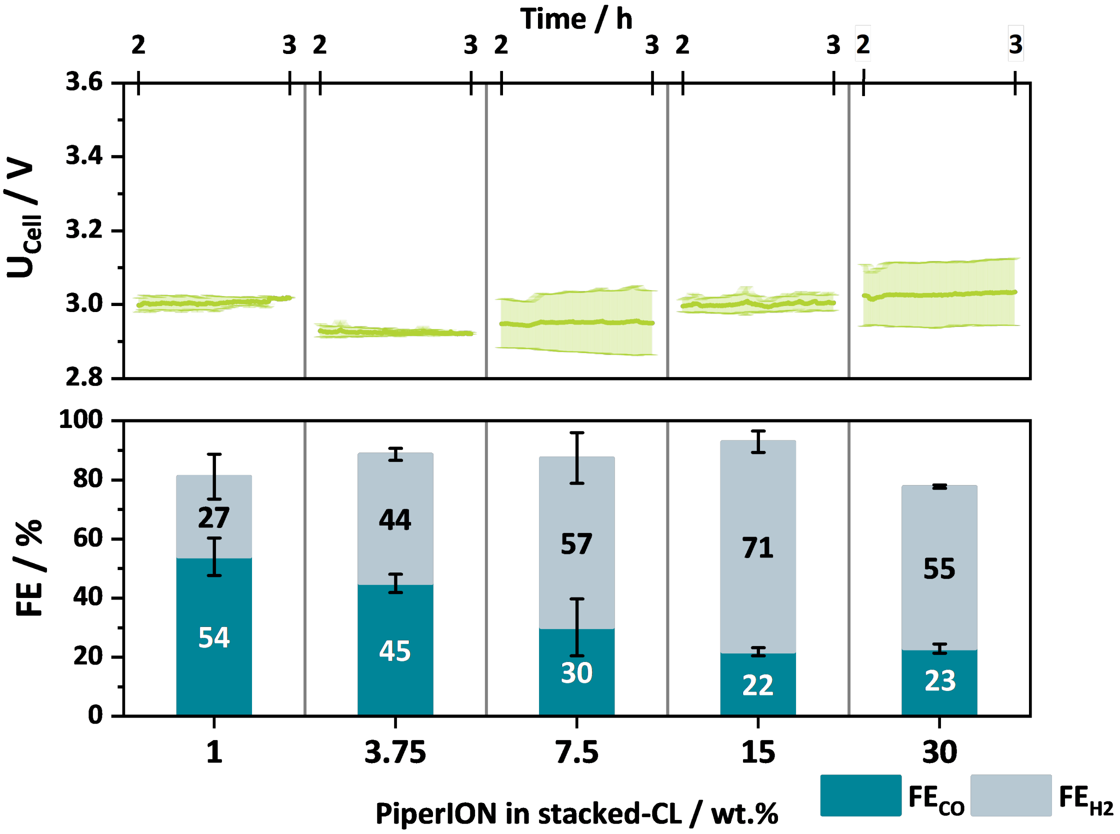

Figure S7: Variation of the added PiperION amount in the ionomer layer of the stacked catalytic layer at 300 mA cm^{-2}. Median data between the 2nd and 3rd hour of electrolysis is shown.

Figure S8: Photograph of the parallel flow fields directly after dissasembling the zero-gap cells after long-term electrolysis

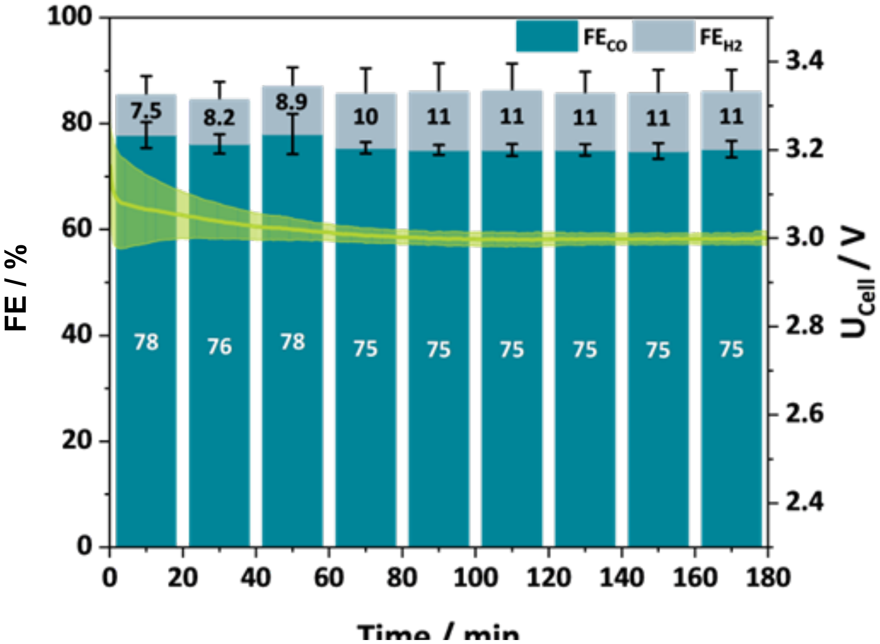

Figure S9: Electrochemical perfomance data for the CO_2R of an improved stacked CL architecture featuring the addition of 20 wt% carbon black in the PTFE-CL.

Table S1: Rheological Analysis: Frequency-Dependent Structural Characteristics of Catalyst Inks. Color Coding: Green - G’’ > G’(Liquid), Red – G’ > G’’ (Solid), Blue – frequency-dependent change from Solid to Liquid

Catalyst Ink Type	**Binder Content [wt.-%]**	**Temperature [°C]**	**Structural Behavior**	**Structural strength G‘ [Pa]**
Piperion	1	25	🟩	
Piperion	1	50	🟩	
Piperion	1	70	🟩	
Piperion	3.75	25	🟥	48
Piperion	3.75	50	🟦	
Piperion	3.75	70	🟩	
Piperion	7.5	25	🟩	
Piperion	7.5	50	🟩	
Piperion	7.5	70	🟩	
Piperion	15	25	🟩	
Piperion	15	50	🟩	
Piperion	15	70	🟩	
Piperion	30	25	🟩	
Piperion	30	50	🟩	
Piperion	30	70	🟩	
PTFE	1	25	🟩	
PTFE	1	50	🟩	
PTFE	1	70	🟩	
PTFE	3.75	25	🟩	
PTFE	3.75	50	🟩	
PTFE	3.75	70	🟩	
PTFE	7.5	25	🟩	
PTFE	7.5	50	🟥	53
PTFE	7.5	70	🟩	
PTFE	15	25	🟩	
PTFE	15	50	🟩	
PTFE	15	70	🟥	1.0
PTFE	30	25	🟩	
PTFE	30	50	🟩	
PTFE	30	70	🟦	

Table S2: BET surfaces of the GDE with different binder proportions of Piperion and PTFE. *These PiperION-based electrodes could not be used for the BET surface area and the low total pore volume.

Sample	**BET-Area / $m^2\ g^{-1}$**
Untreated GDL	9,6
PiperION – 1 wt.%	7,3
PiperION – 3.75 wt.%	*
PiperION – 7.5 wt.%	4,9
PiperION – 15 wt.%	4,7
PiperION – 30 wt.%	*
Sintered GDL	7,6
PTFE – 1 wt.%	6,4
PTFE – 3.75 wt.%	7,4
PTFE – 7.5 wt.%	7,6
PTFE – 15 wt.%	7,3
PTFE – 30 wt.%	7,8

Table S3: Contact angle measurements at different binder amounts. Data with a – denote CLs at which no contact angles could be determined.

Contact Angle / °					
Binder amount / wt.%	1	3.75	7.5	15	30
PiperION-CL	-	-	-	-	-
PTFE-CL	124 ± 3	131 ± 3	147 ± 1	148 ± 5	159 ± 1
Stacked CL-	58 ± 5	-	-	48 ± 7	71 ± 3

References

1 a) P. Jeanty, C. Scherer, E. Magori, K. Wiesner-Fleischer, O. Hinrichsen and M. Fleischer, *Journal of CO_2 Utilization*, 2018, **24**, 454; b) T. Jaster, S. Albers, A. Leonhard, M.-A. Kräenbring, H. Lohmann, B. Zeidler-Fandrich, F. Özcan, D. Segets and U.-P. Apfel, *J. Phys. Energy*, 2023, **5**, 24001;

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