Supplementary Information

Early-Stage Performance Changes of Gas Diffusion Electrodes for CO_2 Electroreduction to Formate

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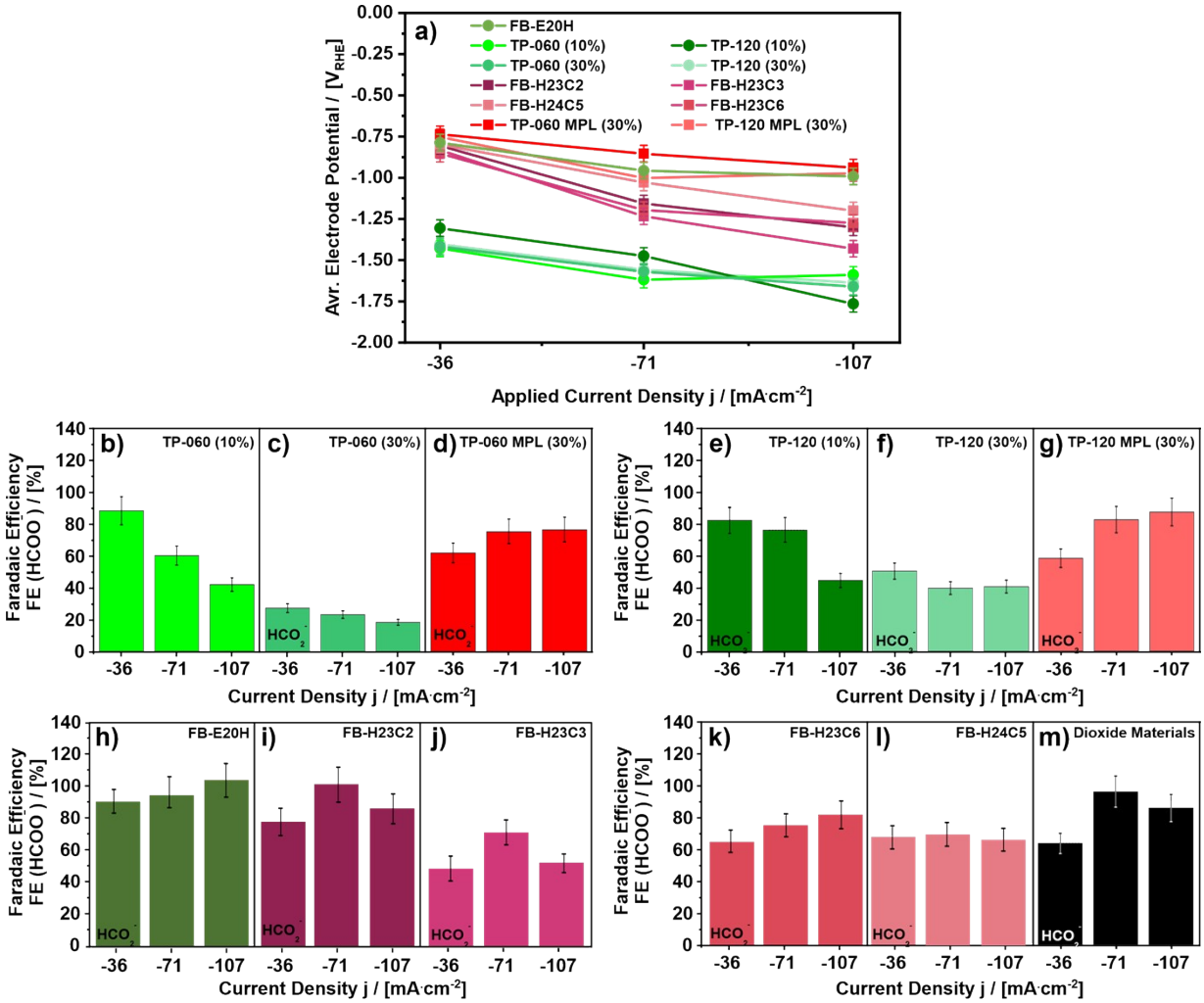

Figure S1: Influence of the GDL on the electrode performance measured via the performance indicators electrode potential (a) and faradaic efficiency (b-m).[1]

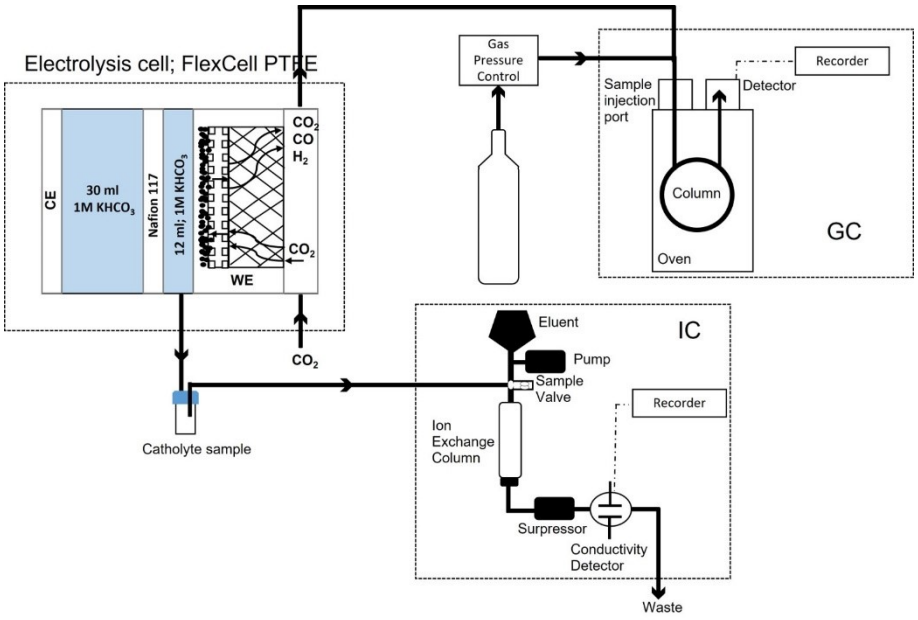

Figure S2: Schematic illustration of the measurement set-up including static GDE test cell (FlexCell), online GC and offline IC.[1]

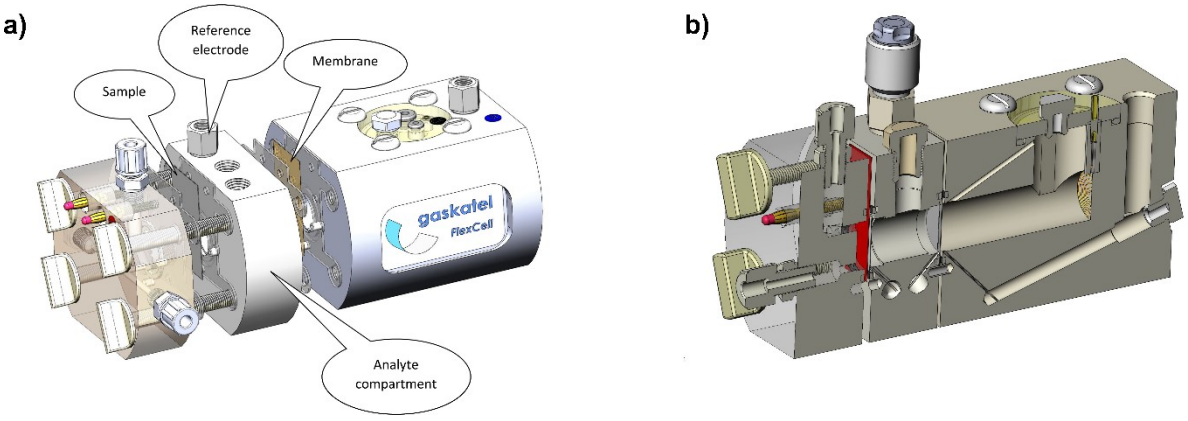

Figure S3: Illustrations of the experimental cell set-up (Flexcell PTFE, Gaskatel, Germany). a) Exterior view. b) Cross section. [2]

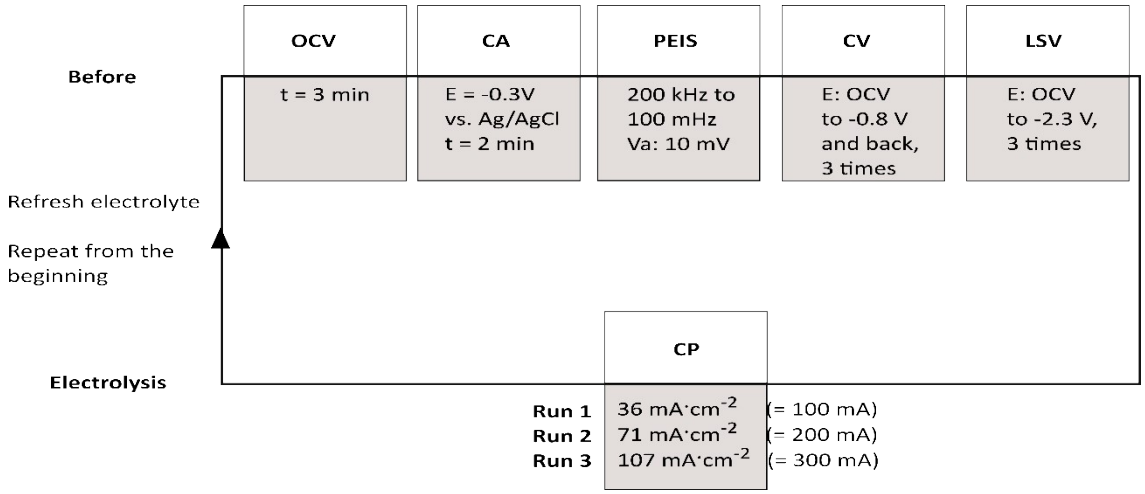

Figure S4: Schematic depiction of the measurement procedure.

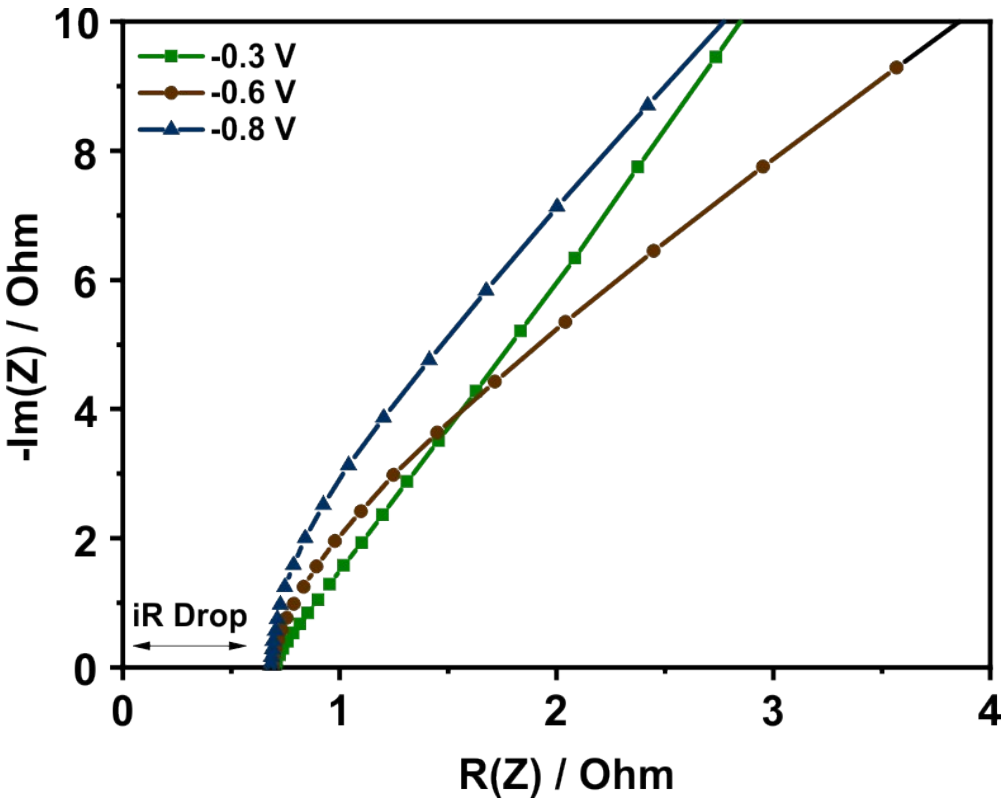

Figure S5: Exemplary Nyquist plots derived by PEIS measurements in the Gaskatel cell set-up. Reference experiment on a silver plate at various electrode potentials.

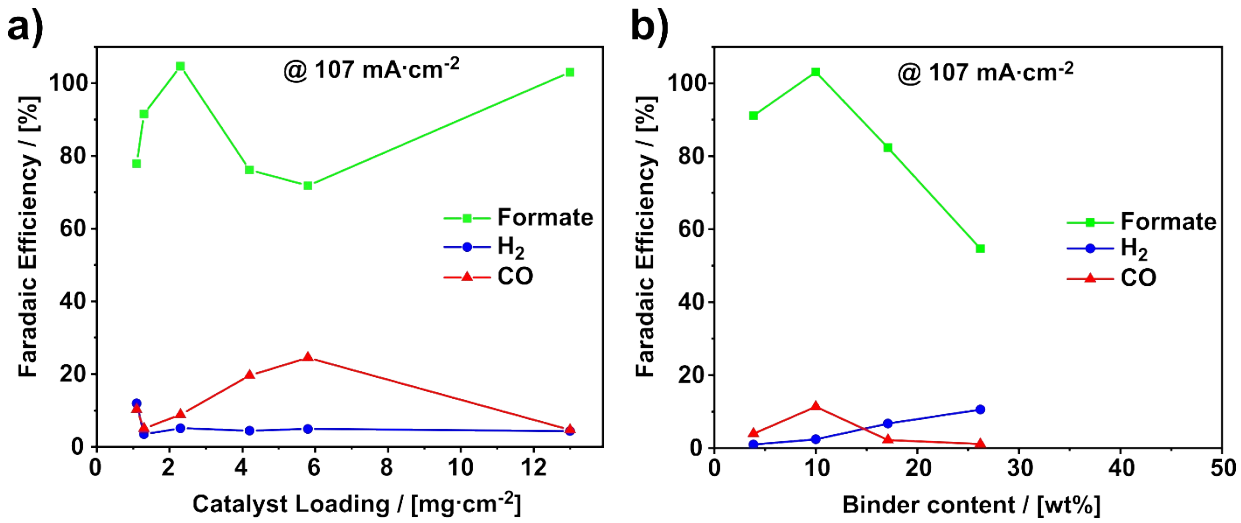

Figure S6: Influence of the catalyst loading (a) and the binder content (b) at the faradaic efficiency of the evolving products. (Catalyst loading: 2.3 mg·cm^{-2}, measurement conditions: batch reactor, 12 ml electrolyte, 1 M $KHCO_3$, continuous CO_2 supply of 20 ml·min^{-1}, start at room temperature, electrolysis time: 45 min each).

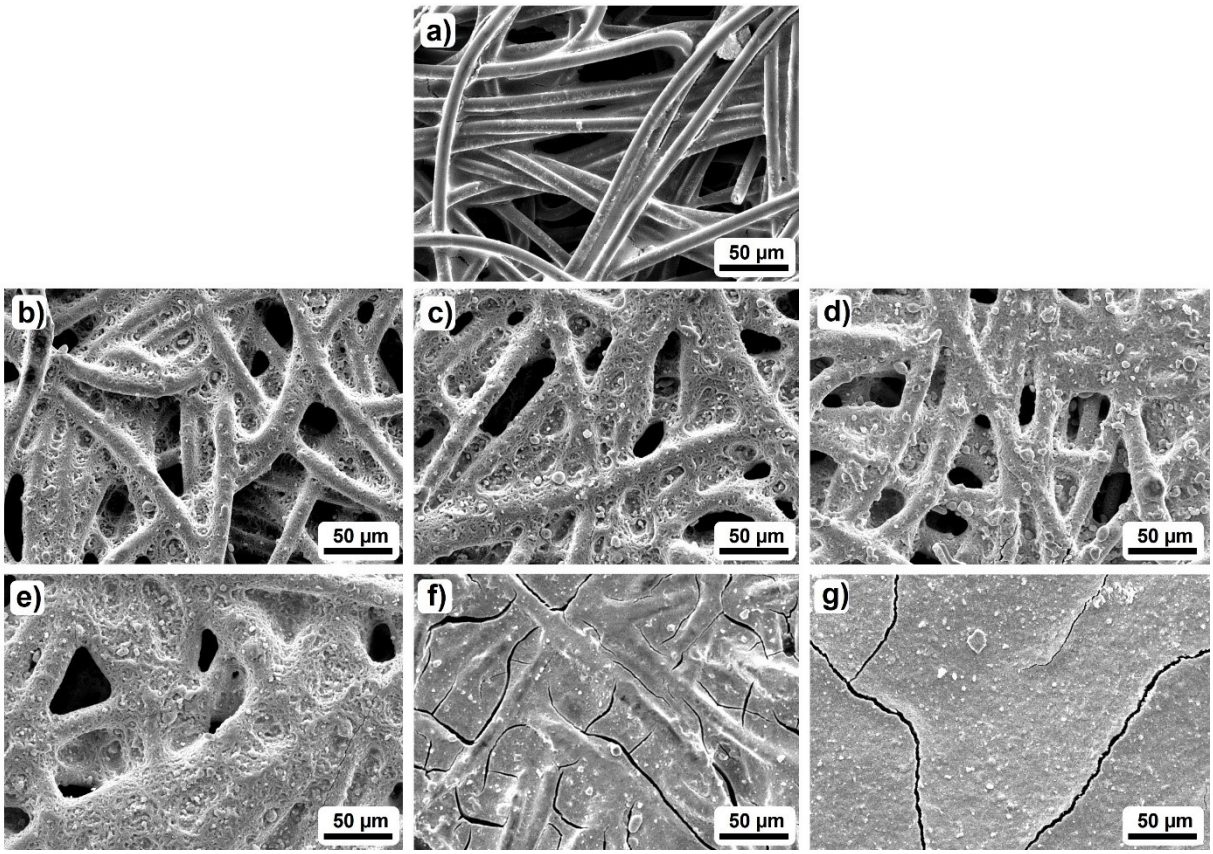

Figure S7: SEM images of the investigated GDEs concerning the influence of the catalyst loading before the electroreduction of CO_2 at 550x magnification, a) Freudenberg E20H GDL, b) 1.1 mg·cm^{-2}, c) 1.3 mg·cm^{-2}, d) 2.3 mg·cm^{-2}, e) 4.2 mg·cm^{-2}, f) 5.8 mg·cm^{-2}, g) 13 mg·cm^{-2}.

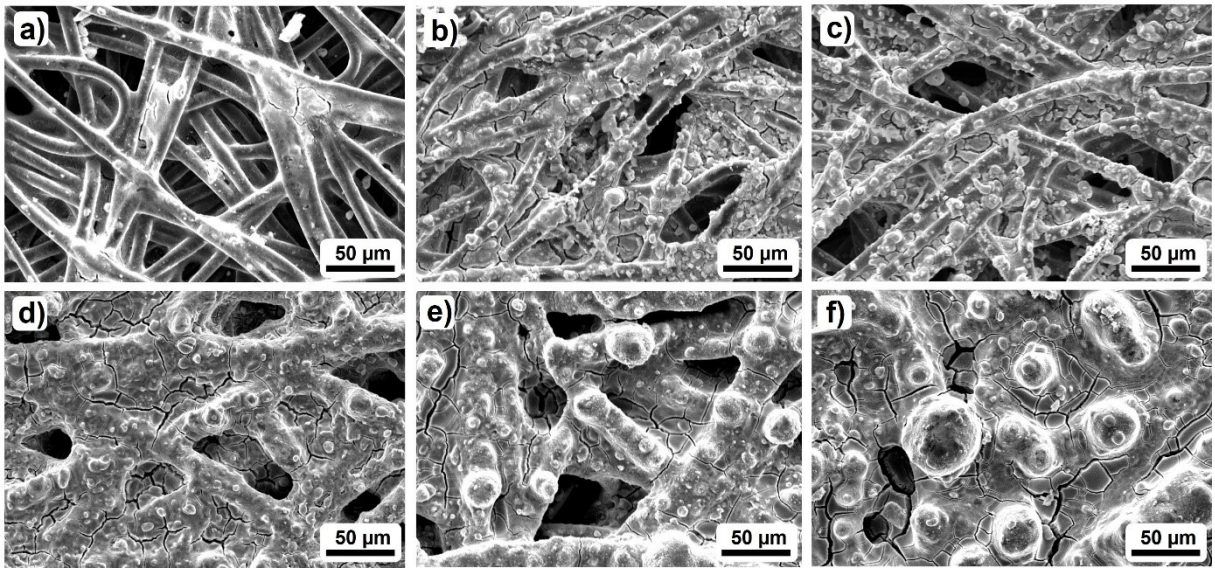

Figure S8: SEM images of the investigated GDEs concerning the influence of the catalyst loading after the first cycle electroreduction of CO_2 at 550x magnification, a) 1.1 mg·cm^{-2}, b) 1.3 mg·cm^{-2}, c) 2.3 mg·cm^{-2}, d) 4.2 mg·cm^{-2}, e) 5.8 mg·cm^{-2}, f) 13 mg·cm^{-2}.

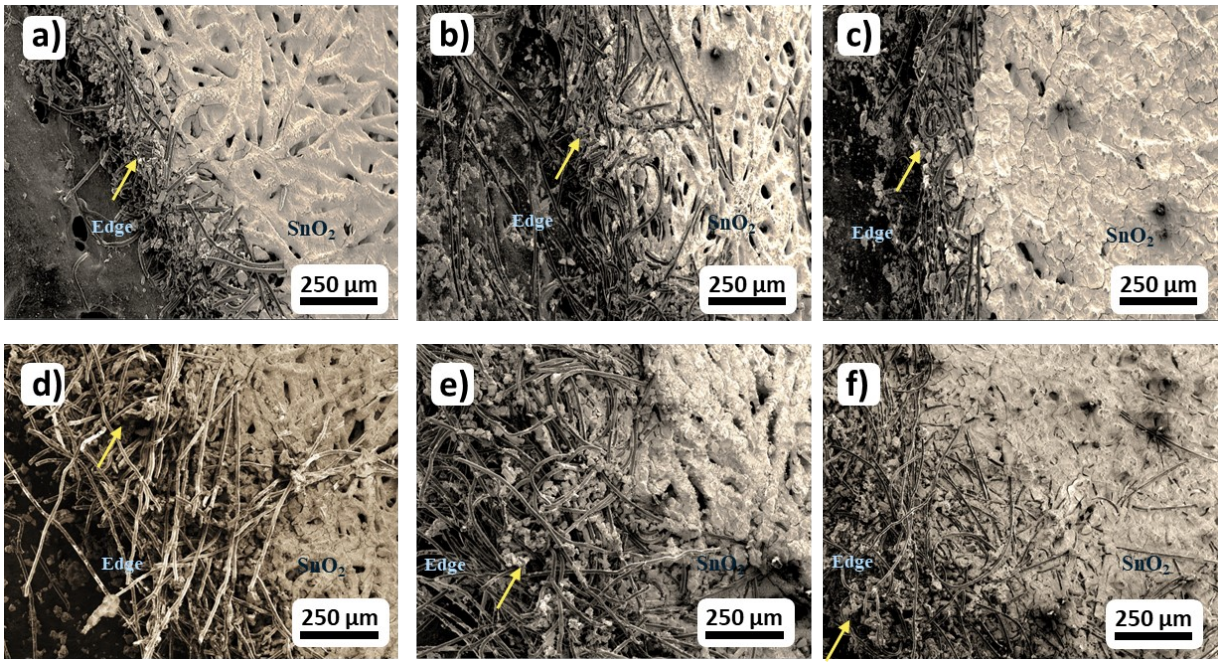

Figure S9: SEM cross sections of the investigated GDEs (catalyst loading > 2.3 $mg \cdot cm^{-2}$) concerning the influence of the catalyst loading in the pristine state and after the first cycle electroreduction of CO_2 at 250x magnification, a),d) 4.2 $mg \cdot cm^{-2}$, b), e) 5.6 $mg \cdot cm^{-2}$ and c), f) 13 $mg \cdot cm^{-2}$. For a better visualization, the fracture edges and the catalyst layer are labelled as edges and SnO_2, respectivley, as well as arrows indicating the catalyst in the deeper layers.

Table S1: Comparison of the contact angles (1M $KHCO_3$) for pristine GDL and GDEs to the GDL with Nafion coating only.

Catalyst loading / [mg·cm^{-2}]	**Contact Angle**			
	GDE (before)		**GDL (Nafion coating)**	
	[°]		**[°]**	
0 (GDL)	137.9°	± 5.0	134.3	± 1.0
1.1	119.9°	± 9.8		
1.3	125.8°	± 4.5		
2.3	126.7°	± 2.7		
4.2	126.4°	± 2.5		
5.8	115.9°	±9.7		
13	123.2°	± 1.6		

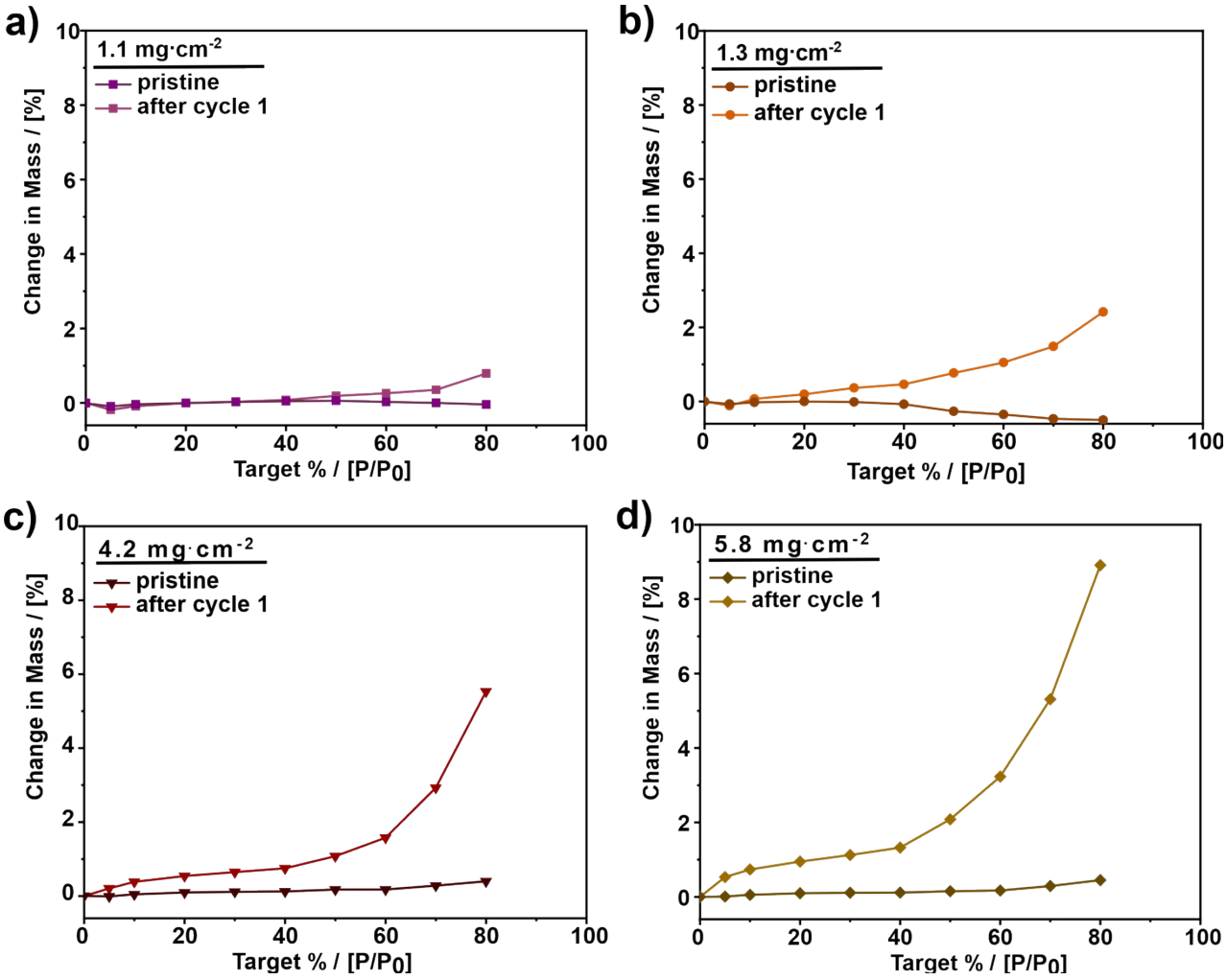

Figure S10: Vapor sorption measurements of GDEs with different catalyst loadings: a) 1.1 mg·cm^{-2} and b) 1.3 mg·cm^{-2}, c) 4.2 mg·cm^{-2} and d) 5.8 mg·cm^{-2}. Moisture adsorption isotherms of the investigated GDEs in different states – pristine and after cycle 1. Vapor sorption measurements were conducted at 25°C with a relative humidity from 0 to 80%, each humidity point was held for 60 min. Negative values are a result of the device uncertainty, common for a small amount of sample with limited adsorption.

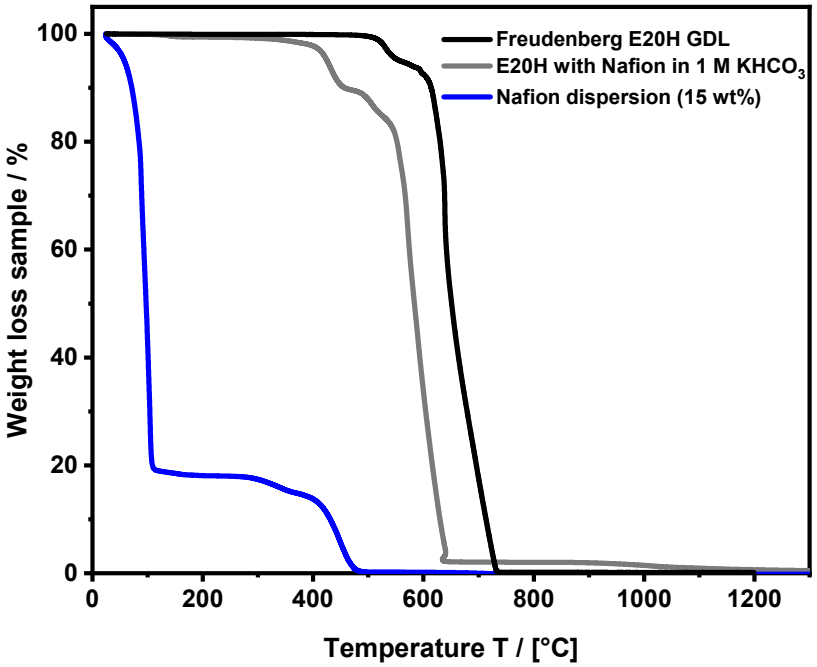

Figure S11: Thermogravimetric analysis of pure Nafion polymer dispersion (15 wt%), the Freudenberg E20H GDL and the Freudenberg E20H GDL coated with Nafion and immersed in $KHCO_3$ for 7 days. TGA was carried out from room temperature to 1200°C with a heating rate of 10 K·min^{-1}, in oxygen environment.

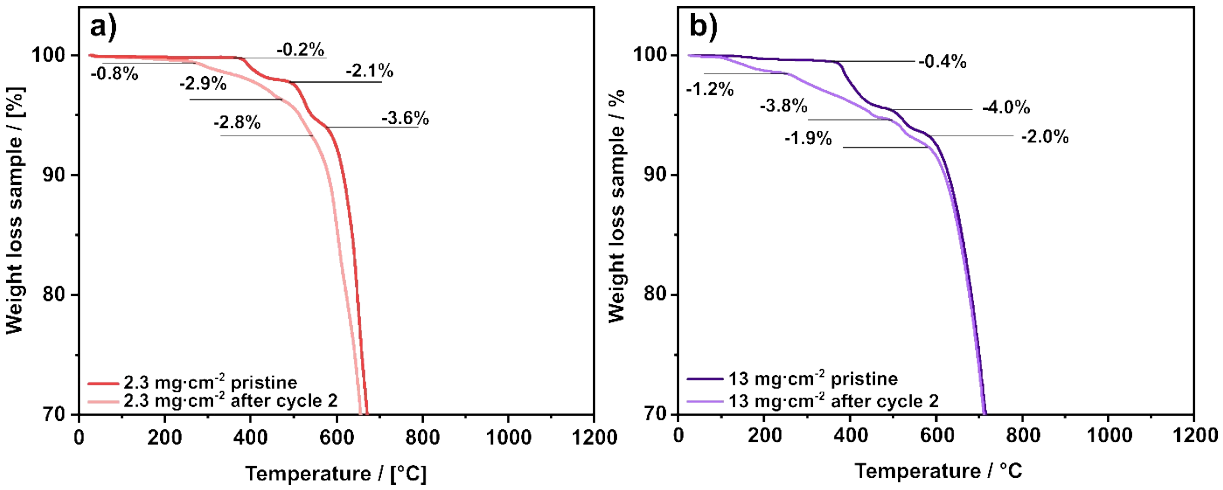

Figure S12: Thermogravimetric analysis (TGA) of the GDEs before and after electroreduction experiments at catalyst loadings of (a) 2.3 mg·cm^{-2} and (b) 13 mg·cm^{-2} in the cut out of 70 – 100wt%. TGA was carried out from room temperature to 1200°C with a heating rate of 10 K·min-1 in oxygen environment.

References

1 V. Theußl, H. Weinrich, C. Heume, K. Dzieciol, B. Schmid, H. Kungl, H. Tempel and R.-A. Eichel, *ChemElectroChem*, 2023, **202300121**, 13.

2 Gaskatel GmbH: www. https://gaskatel.de/shop/elektrochemische-messzelle-betriebsbereit-flexcell-ptfe/. Accessed: 22.08.2023, 16:53