Supporting Information

Scaling Up Electrochemical CO_2 Reduction: Enhancing Performance of Metalloporphyrin Complexes in Zero-Gap Electrolyzers

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Content

S1 Comparison between H-Type and Zero-Gap Cell

Table S1. Comparison between a H-Type cell and a zero-gap cell comprising various important factor for efficient electrochemical CO_2 reduction.

Catholyte	Liquid	Gaseous
Anolyte	Liquid	Liquid
Electrodes	Mostly GCEs and GDEs	GDEs
CO_2 mass transport	Low, limited by solubility of CO_2 in used catholyte Decreases the local CO_2 concentration at the catalytic sites	High, gas stream is immediately fed to the catalytic sites through the GDL Very high local CO_2 concentration
Local pH	Local pH mainly determined by the bulk electrolyte	Very high local pH due to the high current density
In-situ spectroscopy of electrodes	Possible	Not possible yet

Current densities reached	<100 mA/cm^2	>100mA/cm^2
Cell Resistance	High	Low
Scalability	Complicated	Rather easy

S2 Materials and Methods

Synthesis of M(TPP)
All used chemicals were bought from commercial vendors and used without further purification. 5,10,15,20-meso-Tetrakisphenylporphyrin was bought from Thermo Fisher Scientific. The corresponding metal complexes **Fe(TPP)**[1], **Co(TPP)**[2], **Ni(TPP)**[3], **Cu(TPP)**[4], **Zn(TPP)**[3] and **Ag(TPP)**[5] were synthesized according to known procedures and successful product formation was verified via ESI MS.

Electrode Preparation
A catalytic ink was prepared by sonicating 2.5 mg of **M(TPP)**, 5 mg carbon support (either SuperP carbon black or MWCNTS, diameter of xx nm purchased from TCI) and 50 μL Sustainion XA-9 Binder (5 wt% solution in EtOH, purchased from Dioxide Materials) in 2 mL of EtOH for 30 min. Following the catalytic ink was drop casted onto circular carbon cloth gas diffusion layers (diameter of 1.6 cm, purchased from Freudenberg) at a temperature of 90 °C. Drop casting was performed by dropping the ink in 100 μL steps evenly onto the carbon cloth until the desired loading of 1.5 mg per electrode was reached which was controlled via weighing before and after drop casting.

Electrochemistry
Electrocatalysis was performed in an in-house built zero-gap electrolyzer consisting of stainless-steel endplates, insulation plates made from PTFE (1 mm thickness), copper current collectors, titanium-based flow fields (linear for anode side, serpentine for cathode side) and PTFE gaskets to hold the electrodes in place. The cell was tightened with a torque to 5 Nm. During all measurements a PiperION membrane (40 μm thickness, bought from Versogen, soaked in 1 M KOH for 24 h prior to use) was used. All aqueous solutions were prepared with HPLC grade water. In all experiments untreated Ni foam (thickness >2 mm, diameter 1.6 cm^2, bought from Goodfellow) was used as anode. As anolyte 1 M KOH was cycled using a peristaltic pump (GILSON Minipuls3) with a speed of 20 mL/min. The CO$_2$ gas stream (diluted with 2 mL N$_2$, total flow of 22 mL) was humidified *via* purging through HPLC grade water prior to the cell inlet. A GAMRY Reference 1010B potentiostat was used during all electrochemical experiments. Prior to electrocatalysis the catalytic GDE is in-situ activated by applying current densities of 10 mA/cm^2, 20 mA/cm^2, 30 mA/cm^2, 40 mA/cm^2 and 50 mA/cm^2 for one minute each. Afterwards a chronoamperometric measurement at 50 mA/cm^2 for 60 min was performed, followed by a second conditioning period at 100 mA/cm^2 and a subsequent chronoamperometric measurement at 100 mA/cm^2 for 60 min. Each electrode compositions was tested three times.

Gas Chromatography
The outlet gas stream of the cell was connected to an Agilent Technologies 7820A gas chromatograph equipped with two columns (HP-Plot Q and a HP-Molsieve 5 Å column for

the) for product separation and a flame ionization detector (FID),a thermal conductivity detector (TCD) and a Ni-based methanizer. Argon was used as carrier gas. The sample flow towards the column was regulated by a *Bronkhorst EL-FLOW* mass flow controller (1.67 mL/min). During every catalysis each 30 min the product gas composition was injected into the gas chromatograph.

SEM/EDX Measurements

Scanning electron microscopy (SEM) was either performed on ZEISS Gemini 2 Merlin HR-FESEM equipped with an OXFORD AZtecEnergy X-ray microanalysis system for energy dispersive X-ray spectroscopy (EDX) or a ThermoFischer Dualbeam FIB-SEM SCIO2 machine equipped with an Ultimax silicon drift detector (170 mm^2, Oxford Instrument) for EDX measurements. SEM images were recorded with an acceleration voltage of 5 kV.

XPS Measurements

The X-ray photoelectron spectra of the electrodes used in this work were acquired using a Nexsa G2 Surface Analysis System (ThermoFischer) with monochromated and microfocused Al Kα-rays. The detector was 128-channel together with a 180°, double-focusing, hemispherical analyzer. All samples were analyzed with a bandpass energy of 50.00 eV and the resulting peaks were fitted using the software CasaXPS 2.4.24. A Shirely-type background and a Lorentzian lineshape were applied. Each spectrum was calibrated against adventitious carbon, which was set to 284.8 eV. Peaks that were not assigned as satellite peaks were limited to a full width at half maximum of 2.0 eV.

S3 Detailed Catalysis Results

Table S1. Averaged FEs for H₂, CO and CH₄ over the duration of 2 h of catalysis when an electrode with 0.25 mg/cm² of catalyst and 0.5 mg/cm² of carbon black was used.

	50 mA/cm²						100 mA/cm²					
	30 min			60 min			90 min			120 min		
	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄
Fe	99.4±10.2	7.0±1.6	0	109.2±5.6	3.9±1.8	0	104.9±9.1	1.3±0.4	0	105.0±12.3	0.8±0.2	0
Co	34.5±1.7	61.3±0.1	0	22.9±1.0	74.9±0.8	0	39.4±0.7	56.3±2.3	0	55.0±0.5	40.5±0.2	0
Ni	97.9±1.7	6±2.2	0	98.8±1.2	7.4±1.3	0	98.0±1.1	4±1.1	0	100.6±1.4	2.9±1.3	0
Cu	87.9±3.6	13.1±4.7	6.4±0.5	91.9±4.7	11.2±3.6	6.1±0.3	94.5±2.4	6.6±2.3	3.8±0.2	98.7±2.5	4.3±1.7	2.4±0.2
Zn	56.5±7.7	40.3±4.9	0	60.4±8.2	37.3±2.9	0	65.0±10.3	32.7±5.5	0	70.2±19.2	19.4±3.3	0
Ag	3.9±0.3	98.4±0.7	0	3.8±0.7	99.3±1.9	0	3.5±1.9	98.6±1.3	0	7.1±2.2	92.7±0.7	0
TPP	103±2.5	1.0±0.6	0	104.5±4.8	0.8±0.5	0	100.0±1.5	0.6±0.4	0	99.7±0.9	0.6±0.3	0

Table S2. Averaged FEs for H₂, CO and CH₄ over the duration of 2 h of catalysis when an electrode with 0.25 mg/cm² of catalyst and 0.5 mg/cm² of CNTs was used.

	50 mA/cm²						100 mA/cm²					
	30 min			60 min			90 min			120 min		
	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄
Fe	94.2±9.1	6.9±0.9	0	99.2±6.2	4.1±0.4	0	101±1.9	1.27±0.2	0	102.5±2.3	0.7±0.2	0
Co	41.9±5.7	62.7±5.1	0	41.9±2.7	59.6±7.5	0	50.2±6.2	50.8±11.6	0	60.6±3.9	38.8±7.6	0
Ni	98.3±1.5	1.9±0.2	0	95.1±3.3	1.9±0.3	0	97.9±5.7	1.1±0.2	0	96.9±0.6	0.61±0.2	0
Cu	105.75±1.9	1.2±0.3	1.7±0.3	107.5±4.4	0.74±0.01	1.76±0.4	102.67±4.3	0.5±0.1	1.0±0.2	106.0±3.7	0.3±0.1	0.5±0.2
Zn	73.7±1.3	35.5±3.0	0	75.9±0.2	34.6±3.6	0	89.7±3.6	15.9±4.4	0	97.8±3.2	6.6±1.5	0
Ag	6.5±1.2	90.7±6.5	0	13.2±6.3	86.8±9.1	0	45.2±1.3	54.64±3.1	0	54.1±19.40	49.2±23	0

Table S3. Averaged FEs for H₂, CO and CH₄ over the duration of 2 h of catalysis at 10 mA/cm² when an electrode with 0.25 mg/cm² of **Fe(TPP)** and 0.5 mg/cm² of carbon black was used.

	30 min			60 min			90 min			120 min		
	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄	FE H₂	FE CO	FE CH₄
Fe	18.8±1.3	90.67±1.0	0	40.5±8.7	66.4±6.6	0	68.7±2.2	36.3±0.1	0	72.0±11.5	20.9±3.0	0

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S4 SEM data

SEM pictures of each electrode were recorded at three different magnifications. EDX measurements were also performed, however no further information about the electrode compositions were obtained due to the very low complex content compared to the carbon content.
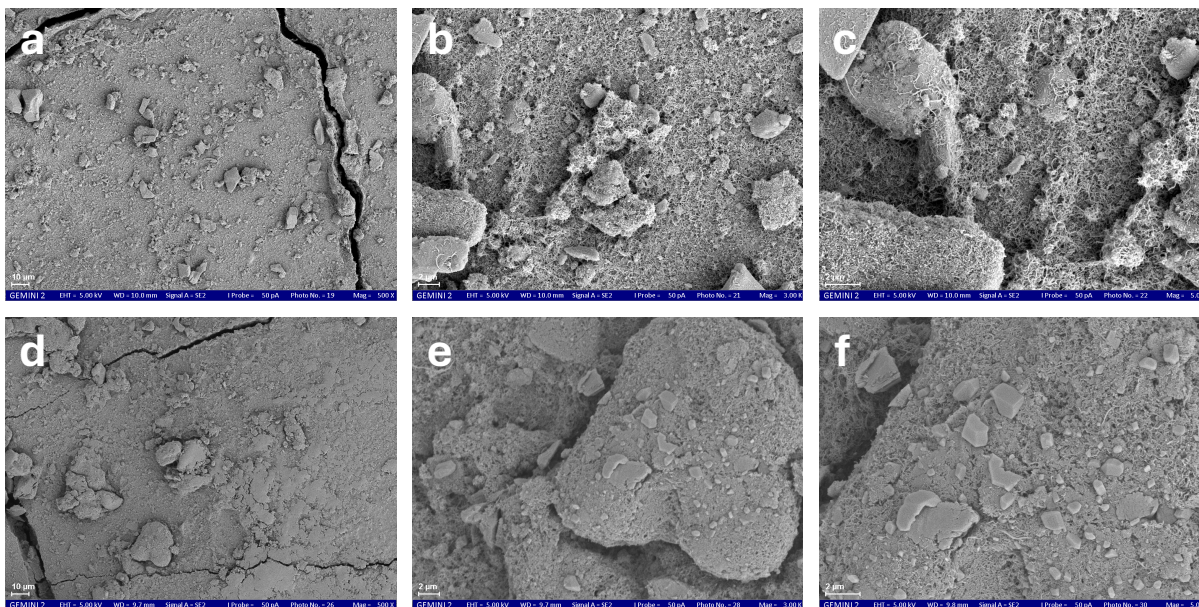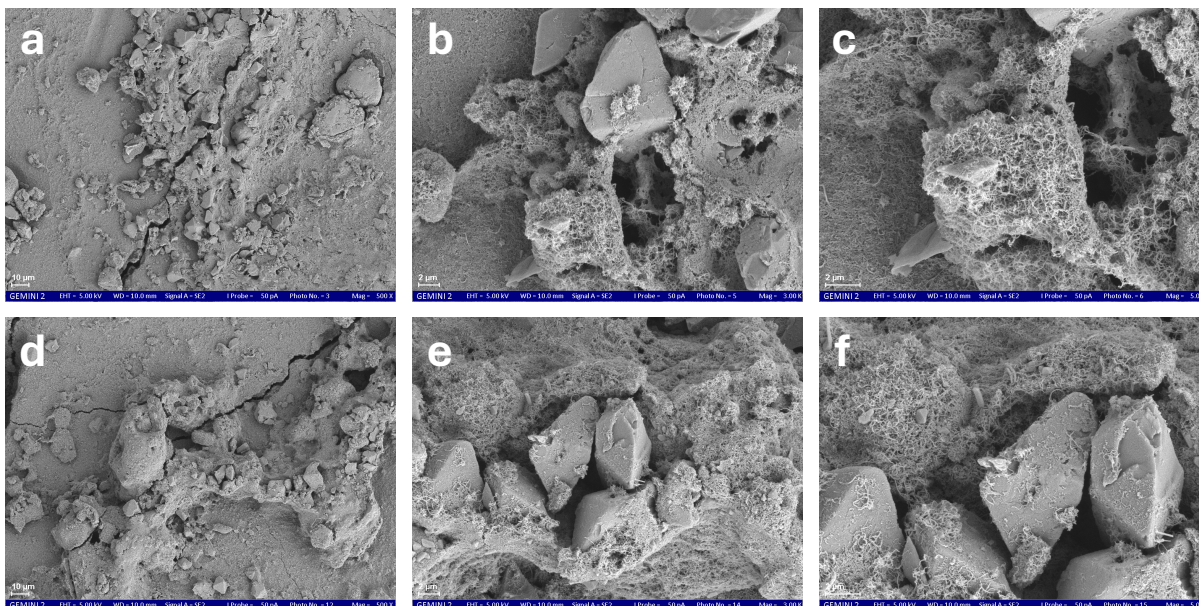

Figure S1.SEM Pictures of an electrode prepared with FeTPP(0. 5mg), MWCNTs (1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.
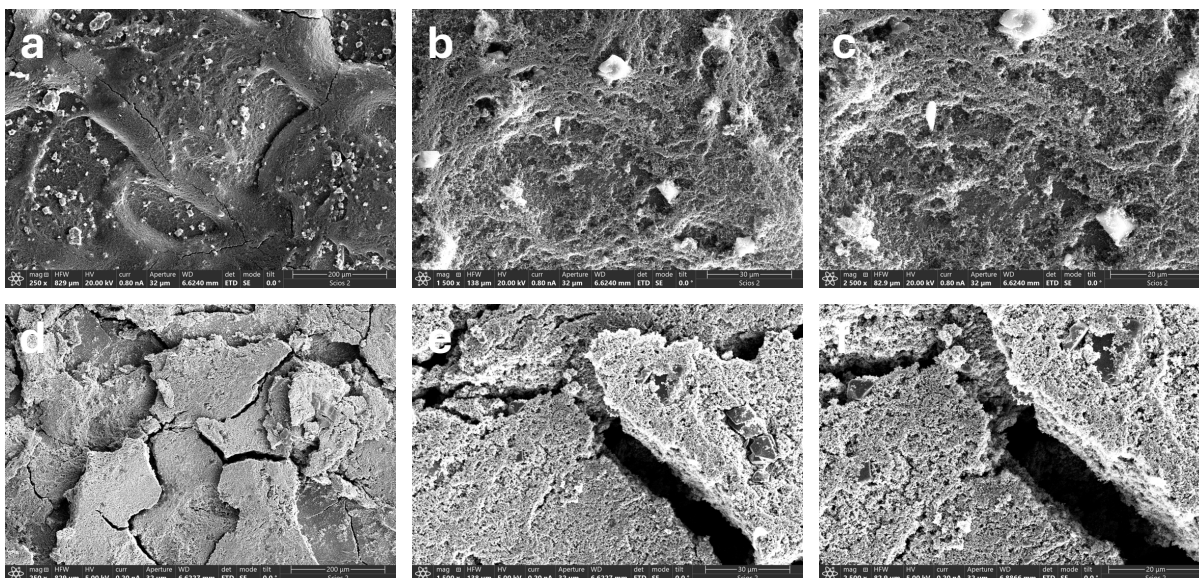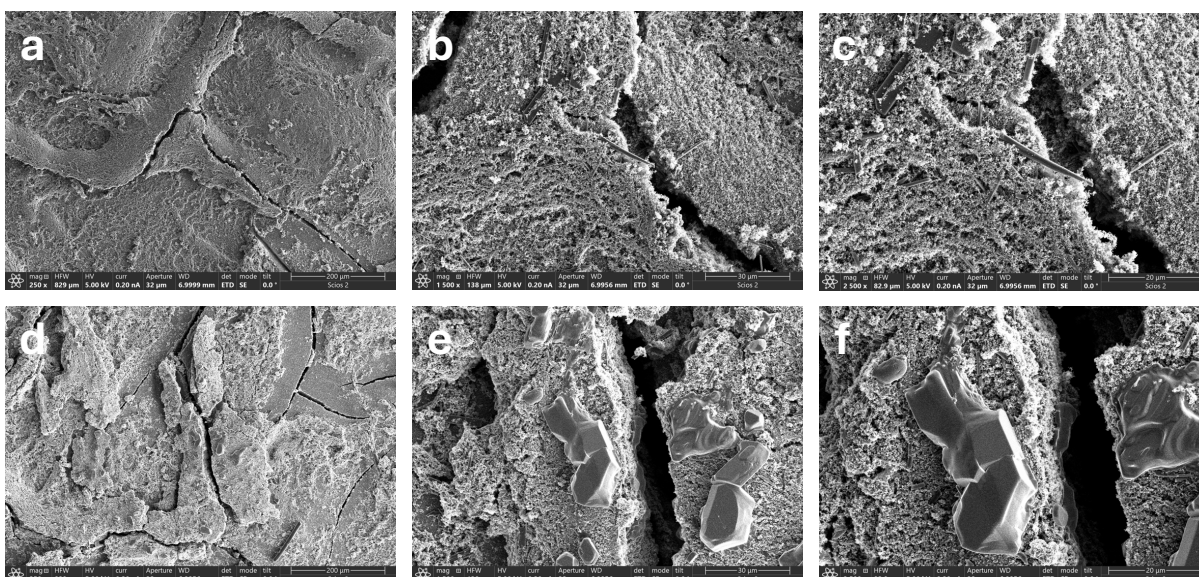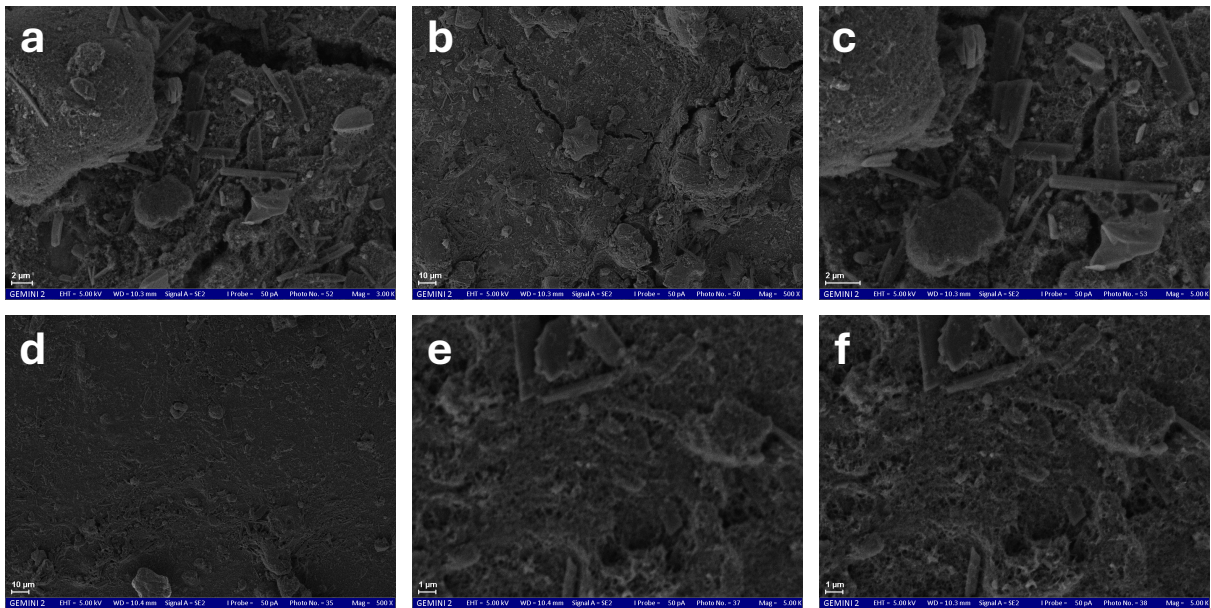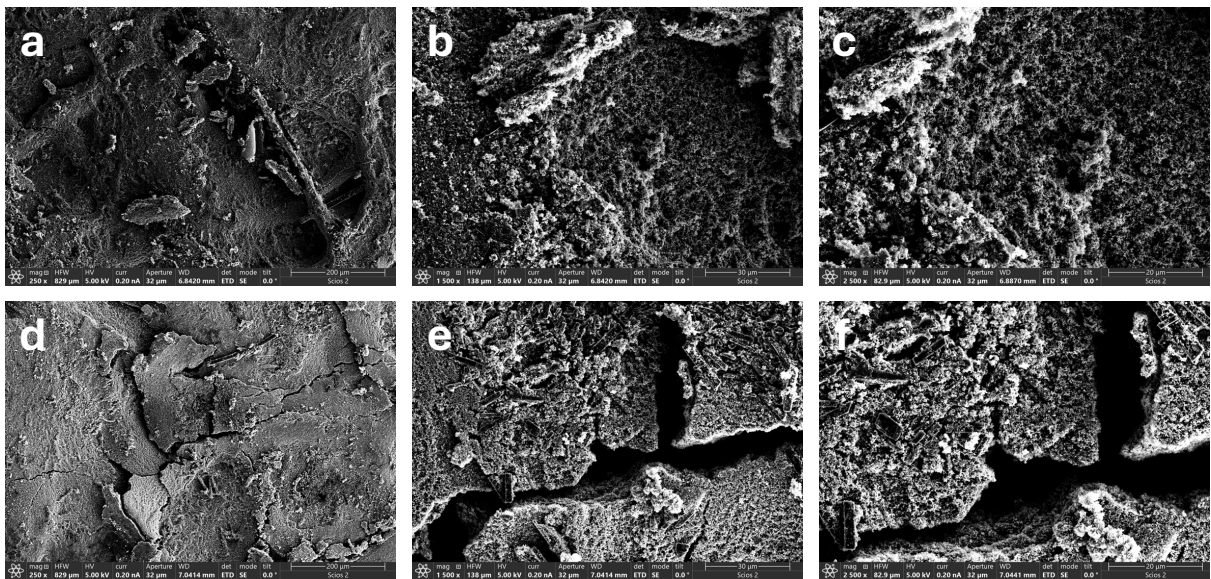

Figure S2. SEM Pictures of an electrode prepared with NiTPP(0. 5mg), MWCNTs (1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.
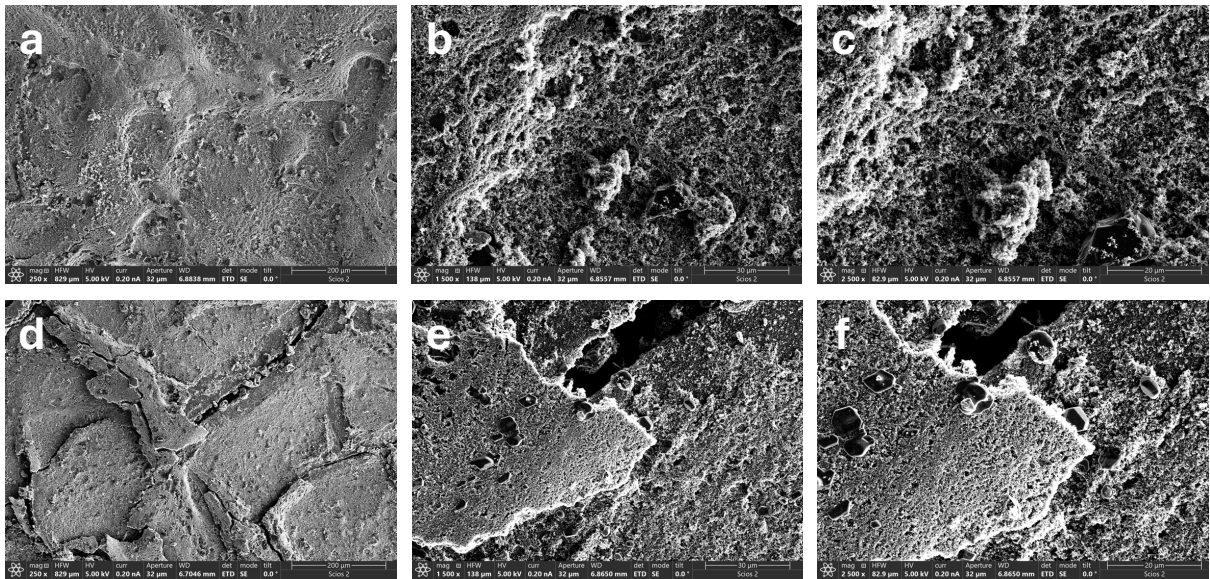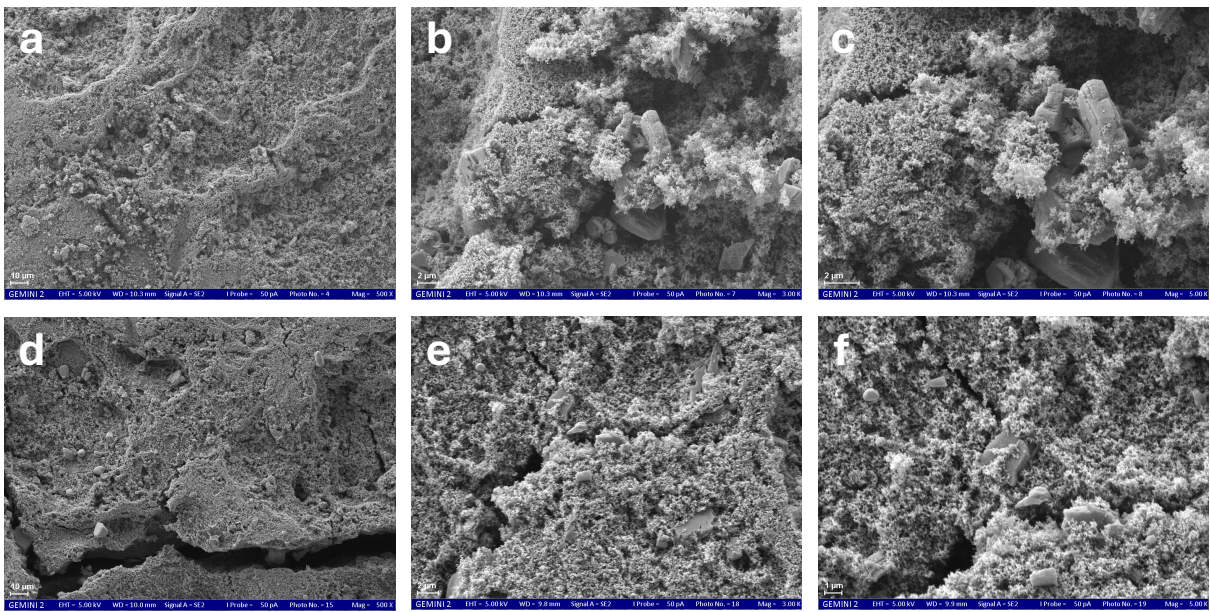
Figure S3. SEM Pictures of an electrode prepared with NiTPP(0. 5mg), SuperP carbon black(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.

Figure S4. SEM Pictures of an electrode prepared with CoTPP(0. 5mg), SuperP carbon black(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.

Figure S5. SEM Pictures of an electrode prepared with CoTPP(0.5 mg), MWCNTs(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.

Figure S6. SEM Pictures of an electrode prepared with ZnTPP(0. 5mg), SuperP carbon black(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.

Figure S7. SEM Pictures of an electrode prepared with CuTPP(0. 5mg), SuperP carbon black(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.

Figure S8. SEM Pictures of an electrode prepared with AgTPP(0. 5mg), SuperP carbon black(1.0 mg) and Nafion Binder at 500x (a, d), 3000x (b, e) and 5000x (c, f) magnification either before (a, b, c) or after (d, e, f) electrolysis.
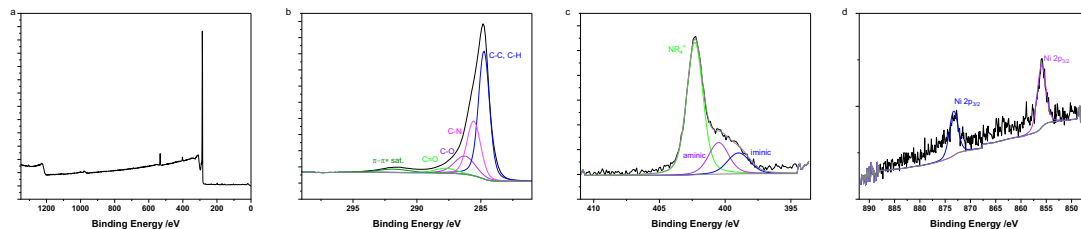
S5 XPS data
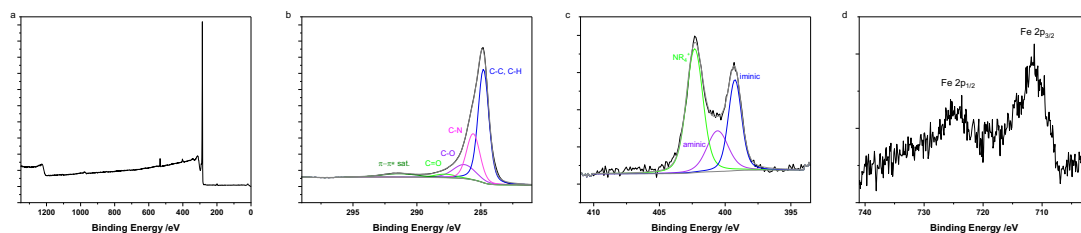
*Figure S9. Acquired XPS spectra for an electrode prepared with **Fe(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) Fe 2p XPS spectrum.*
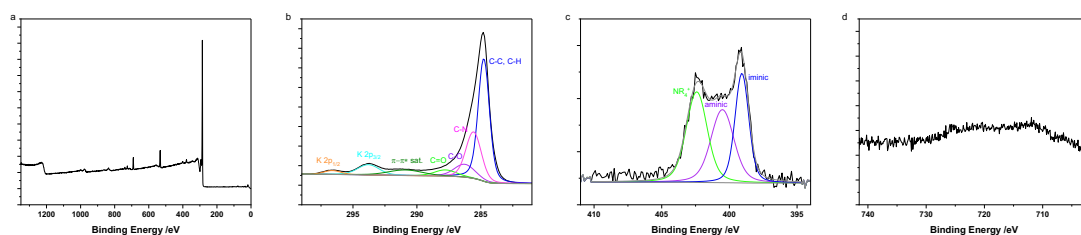
*Figure S10. Acquired XPS spectra for an electrode prepared with **Fe(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder after electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) Fe 2p XPS spectrum: The Cs contamination will have been caused by the anolyte compartment.*

*Figure S11. Acquired XPS spectra for an electrode prepared with **Ni(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) Ni 2p XPS spectrum.*
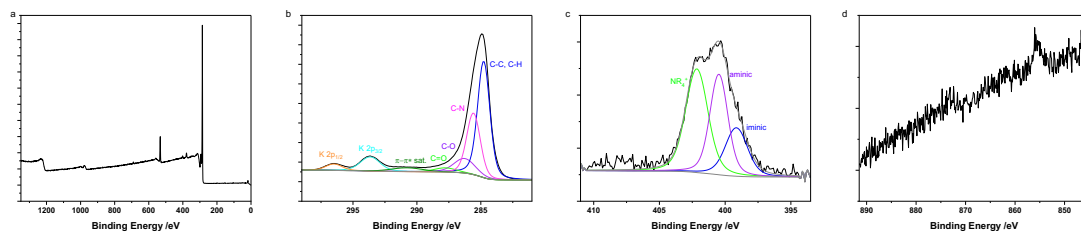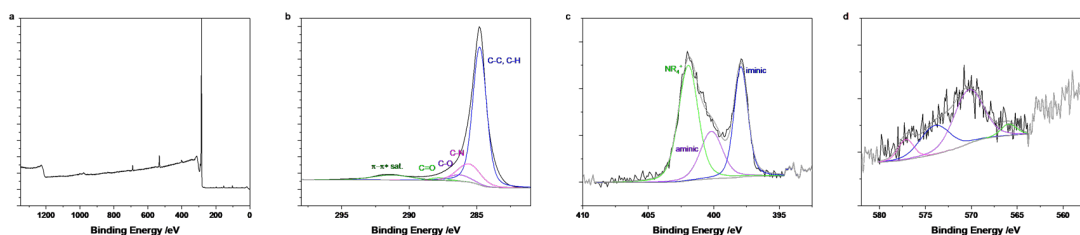

*Figure S12. Acquired XPS spectra for an electrode prepared with **Ni(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 after electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) Ni 2p XPS spectrum.*

*Figure S13. Acquired XPS spectra for an electrode prepared with **Cu(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) spectrum of the Cu Auger peaks.*
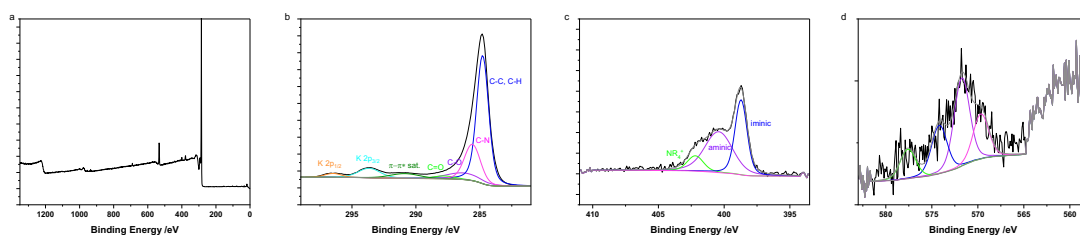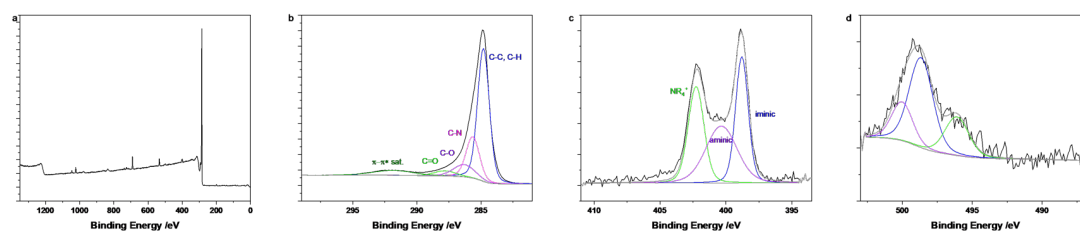

*Figure S14. Acquired XPS spectra for an electrode prepared with **Cu(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder after electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) spectrum of the Cu Auger peaks.*
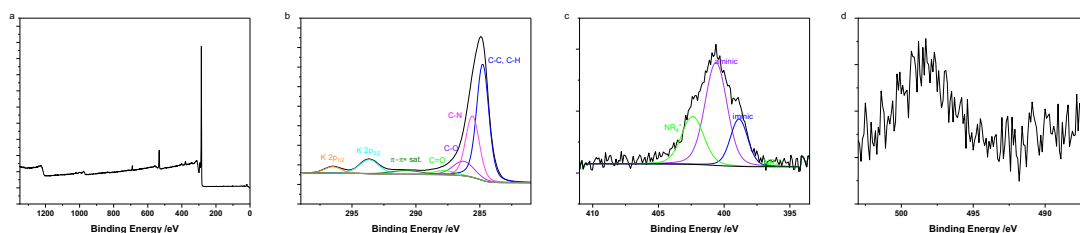

*Figure S15. Acquired XPS spectra for an electrode prepared with **Zn(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) spectrum of the Zn Auger peaks.*

*Figure S16. Acquired XPS spectra for an electrode prepared with **Zn(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 after before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins; d) spectrum of the Zn Auger peaks.*
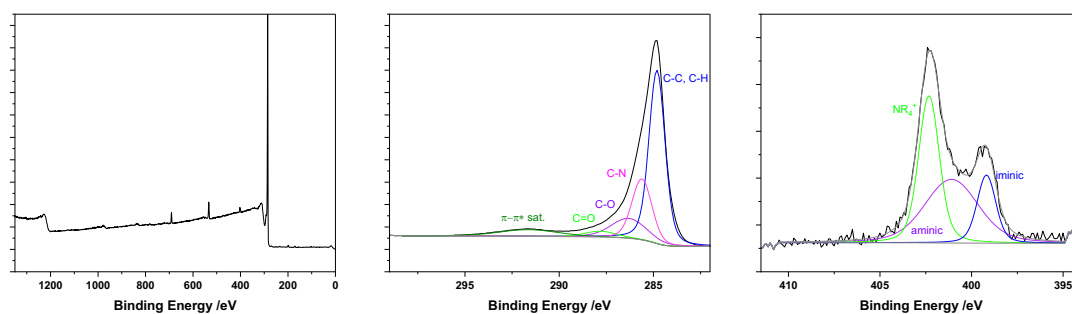
*Figure S17. Acquired XPS spectra for an electrode prepared with **Co(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins.*
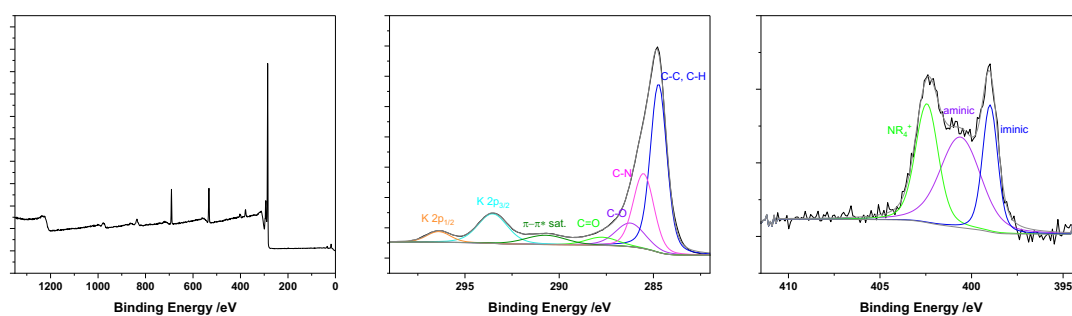

*Figure S18. Acquired XPS spectra for an electrode prepared with **Co(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder after electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins.*
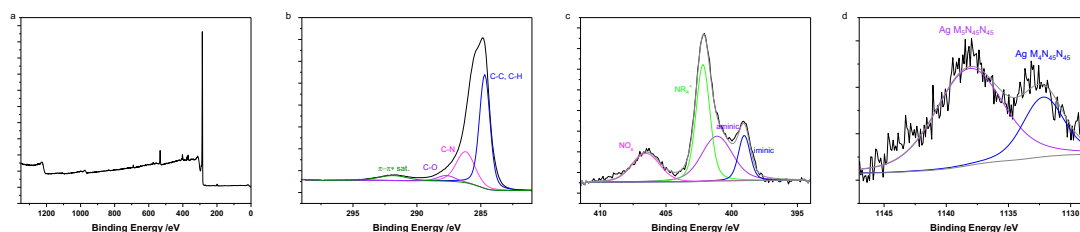

*Figure S19. Acquired XPS spectra for an electrode prepared with **Ag(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder before electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong to the inner core of the porphyrins, NO_x signals are derived from the complex synthesis in which $AgNO_3$ was used as Ag source; d) spectrum of the Ag Auger peaks.*
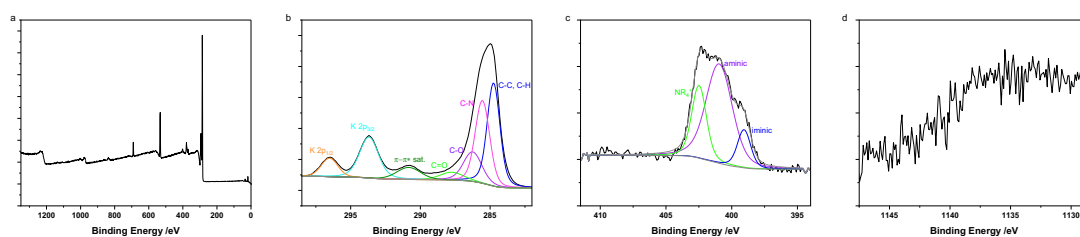

*Figure S20. Acquired XPS spectra for an electrode prepared with **Ag(TPP)** (0.5 mg) and carbon black (1.0 mg) and sustainion XA-9 binder after electrolysis. a) Survey Scan; b) C 1s XPS spectrum; c) N 1s XPS spectrum: The NR_4^+ can be attributed to the binder, the other signals belong of the inner core of the porphyrins; d) spectrum of the Cu Auger peaks.*
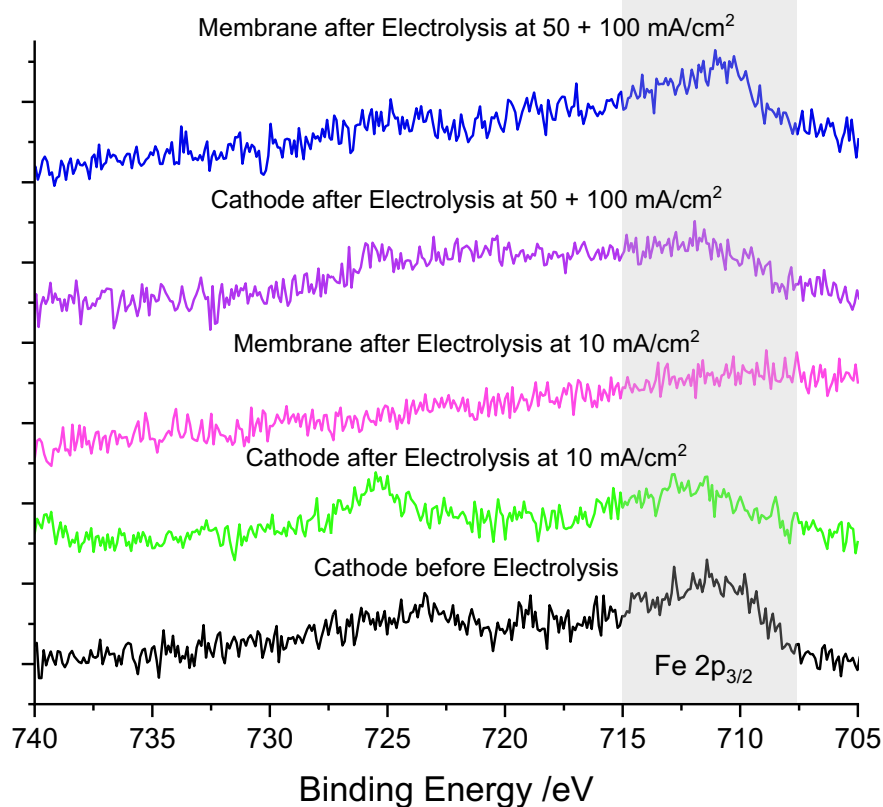
Figure S21Acquired XPS spectra in the area of the binding energy of the Fe 2p orbital of a pre electrolysis cathode (black), a cathode after 2 h of electrolysis at 10 mA/cm^2 (green), a membrane after 2 h of electrolysis at 10 mA/cm^2 (pink), a cathode after 1 h of electrolysis at 50 mA/cm^2 followed by 1h of electrolysis at 100 mA/cm^2 (purple), a membrane after 1 h of electrolysis at 50 mA/cm^2 followed by 1h of electrolysis at 100 mA/cm^2 (blue).

S6 References

[1] Y. Okabe, S. K. Lee, M. Kondo, S. Masaoka J. Biol. Inorg. Chem., 2017, 22, 713-725.

[2] Isaac Kwaku Attatsi, Weihua Zhu and Xu Liang New J. Chem., 2020, 44, 4340-4345.

[3] Sean A. Vail, David I. Schuster, Dirk M. Guldi, Marja Isosomppi, Nikolai Tkachenko, Helge Lemmetyinen, Amit Palkar, Luis Echegoyen, Xihua Chen, and John Z. H. Zhang J. Phys. Chem. B 2006, 110, 29, 14155–14166.

[4] J. Śniechowska, P. Paluch and M. J. Potrzebowski RSC Adv., 2017, 7, 24795-24805.

[5] Man-Ho So, V.A.L. Roy Dr., Zong-Xiang Xu, Stephen Sin-Yin Chui Dr., Mai-Yan Yuen, Chi-Ming Ho Dr., Chi-Ming Che Chem. Asian J. 2008, 3, 1968 – 1978.