Supporting Information: Decoupling Multiscale Morphological Effects in Templated Porous Ag Electrodes for Electrochemical CO_2 Reduction

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1. Cyclic voltammogram of the electrodeposition solution

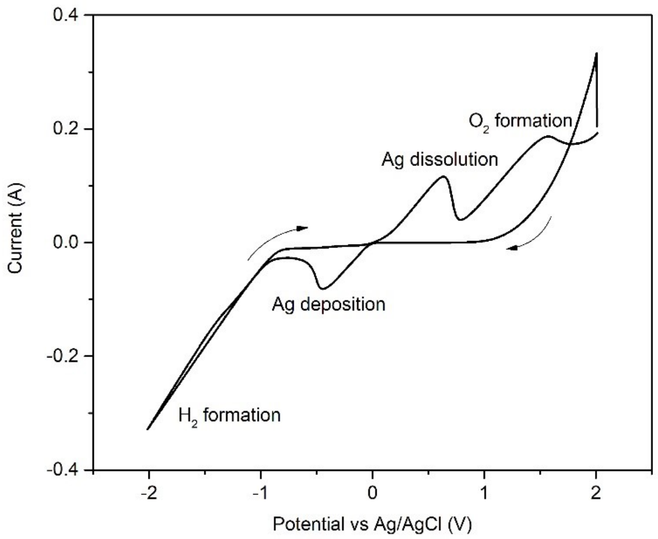


Figure S 1: cyclic voltammogram of the electrodeposition solution consisting of 0.05 M $AgNO_3$, 0.5 M NH_4OH, 1.0 M $NaNO_3$ and 0.01 M EDTA run between 2 V and -2 V vs Ag/AgCl with a scan rate of 0.1 V/s.

2. Schematic illustration of convection, diffusion and the reduction of CO_2

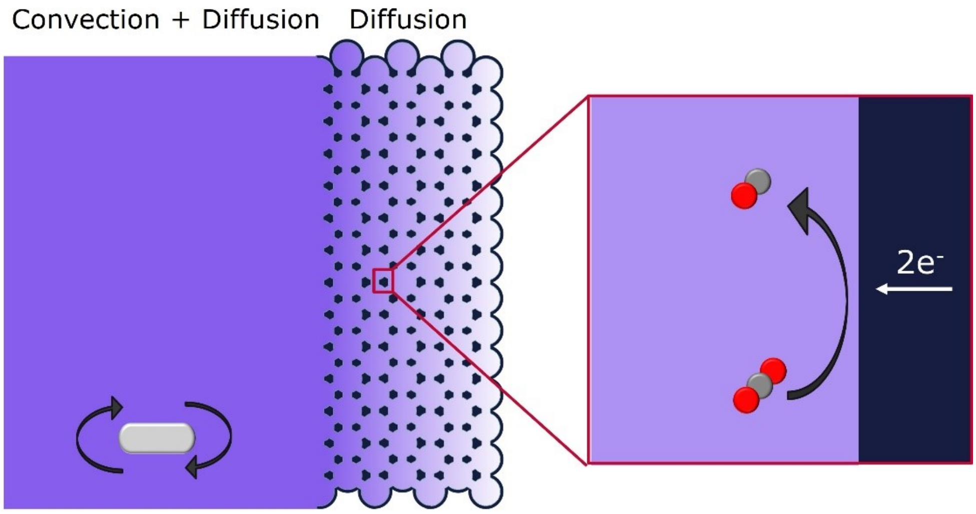


Figure S 2: Schematic representation of convection and diffusion inside the electrochemical cell and the porous electrode including the CO_2 reduction reaction that is taking place.

3. PMMA spheres

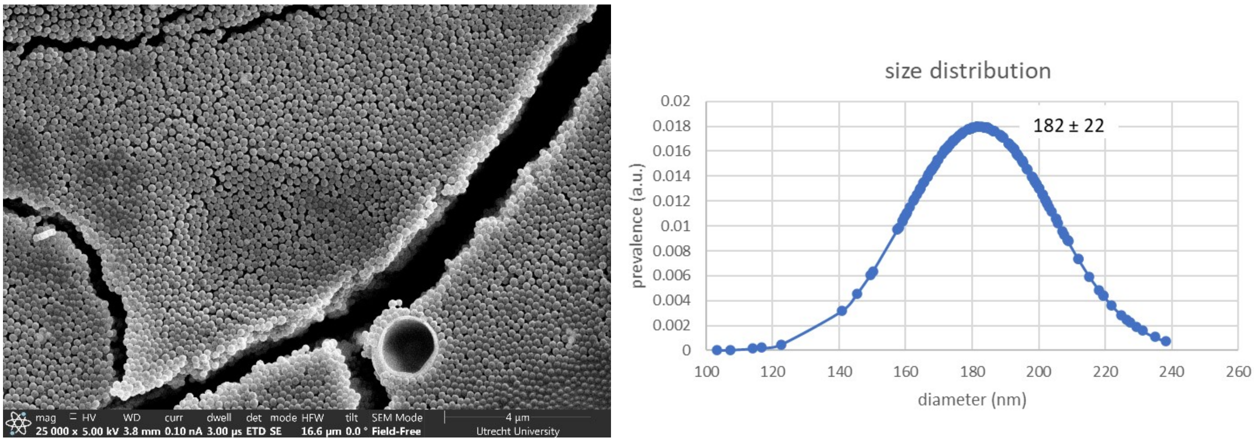


Figure S 3: a) SEM images of the PMMA spheres used in templating; b) size distribution and average diameter of the counted PMMA spheres used for templating

4. Scanning Electron Microscopy Energy-dispersive X-ray Spectroscopy

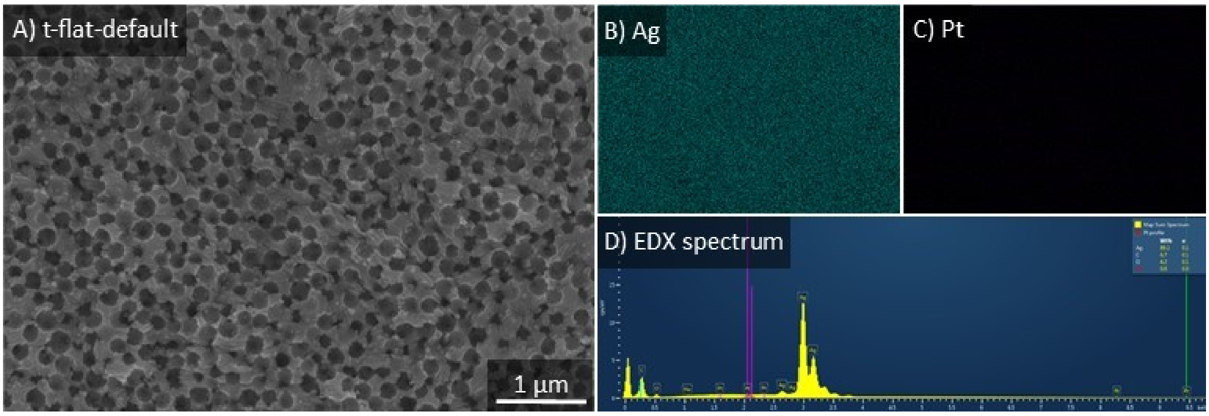


Figure S 4: a) SEM image of the t-flat-default sample, the corresponding EDX maps for b) Ag and c) Pt and the d) the EDX spectrum.

5. X-ray diffraction

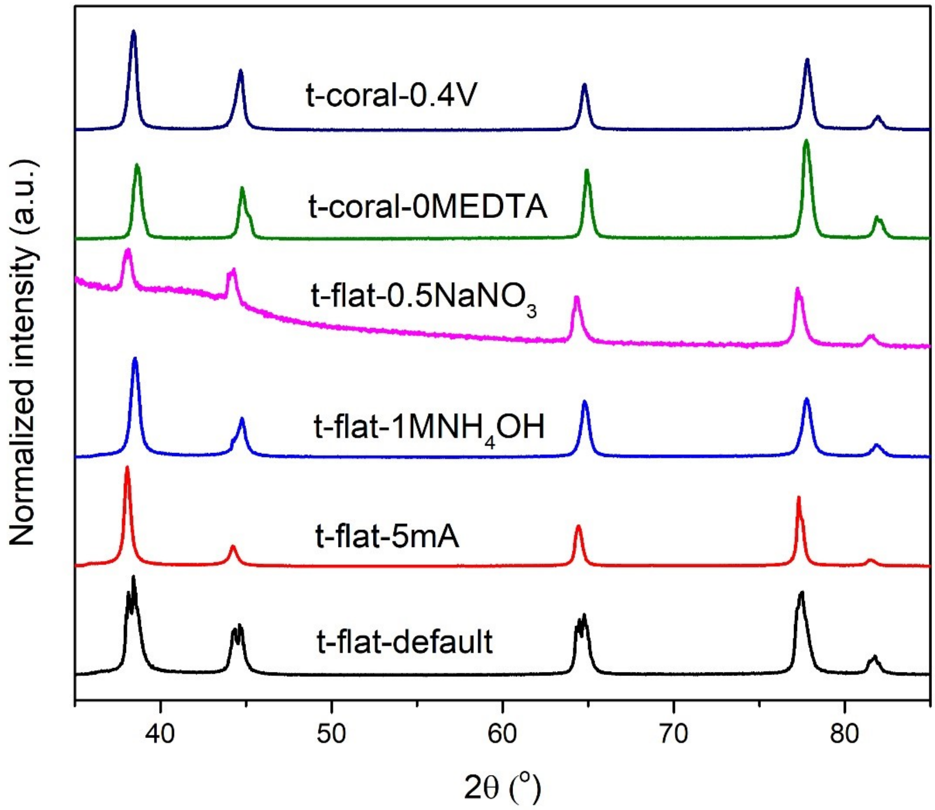


Figure S 5: X-ray diffraction patterns of the t-flat-default, t-flat-5mA, t-flat-1MNH$_4$OH, t-flat-0.5MNaNO$_3$, t-coral-0MEDTA and t-coral-0.4V electrodes.

6. X-ray photoelectron spectroscopy

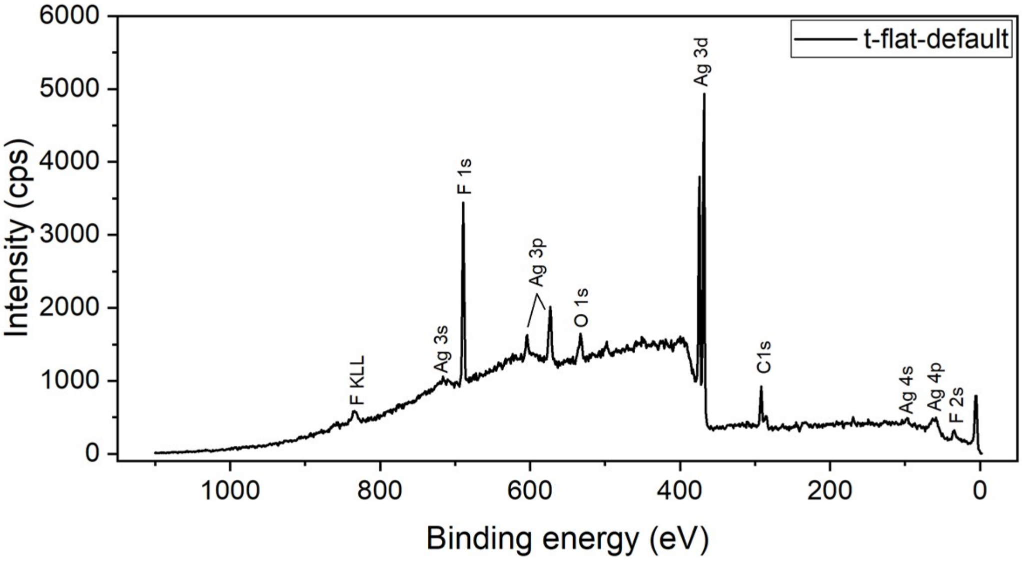
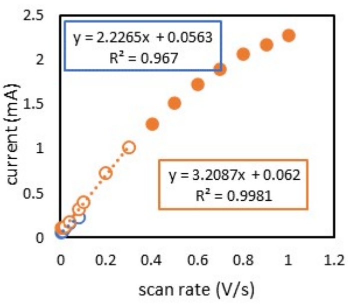
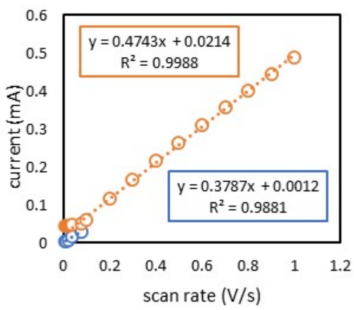
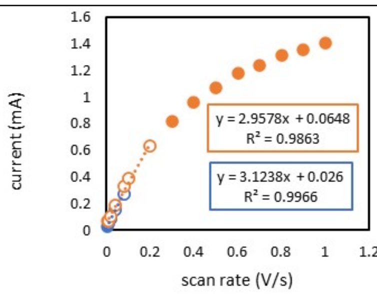
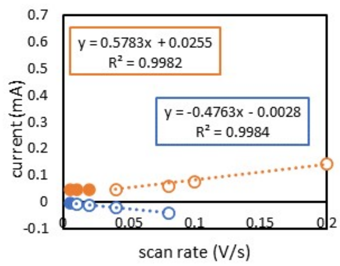


Figure S 6: X-ray photoelectron spectroscopy survey spectrum (Al Kα radiation, Epass=100 eV) of the t-flat-default electrode, indicating the presence of Ag, C, O and F.

7. Double layer capacitance

	Templated	Non-templated
Default		
-5mA		

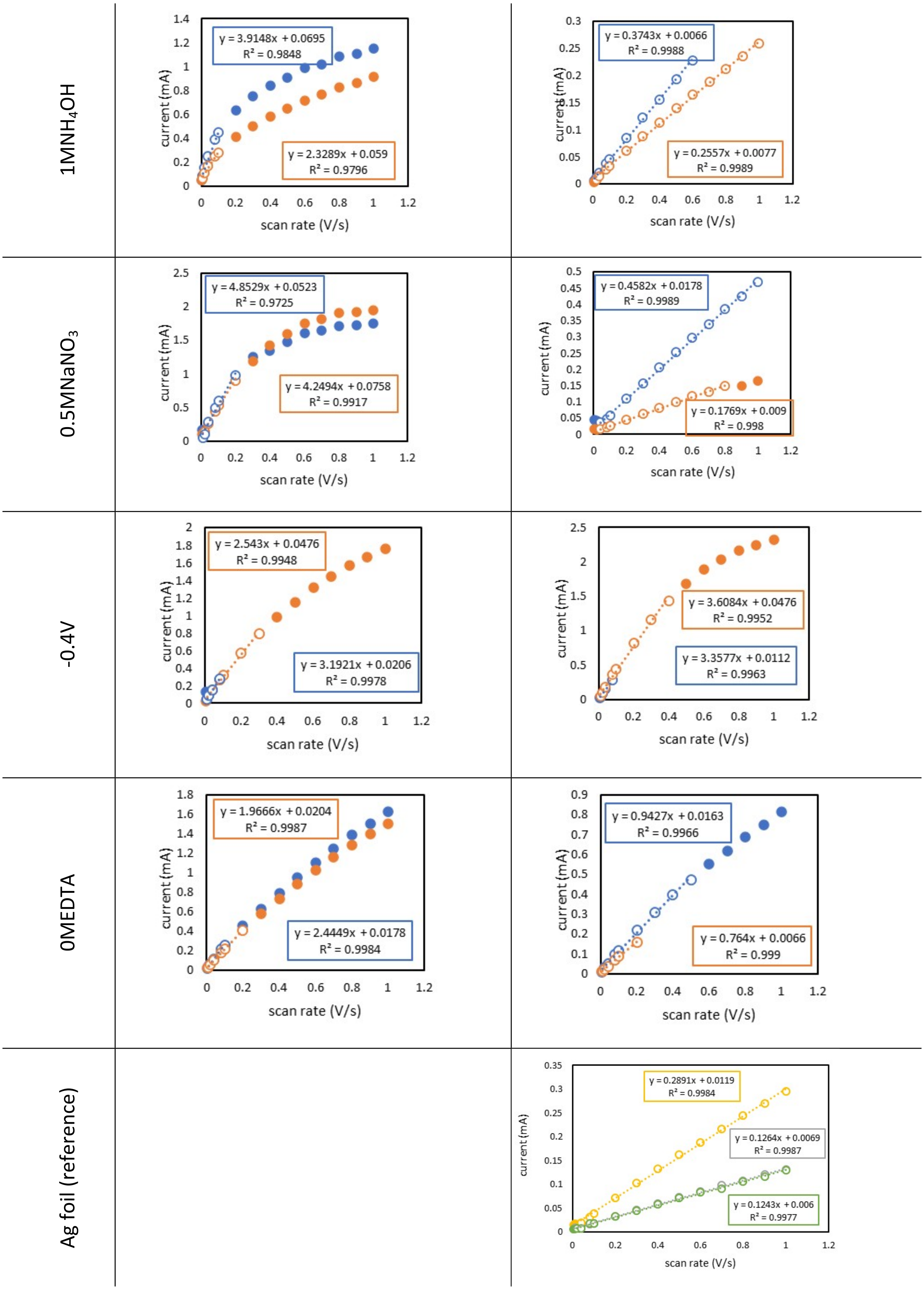


Figure S 7: Figure S 3:DLC graphs of all (non)-templated electrodes. The open dots indicate the data included to fit the double-layer capacitance.

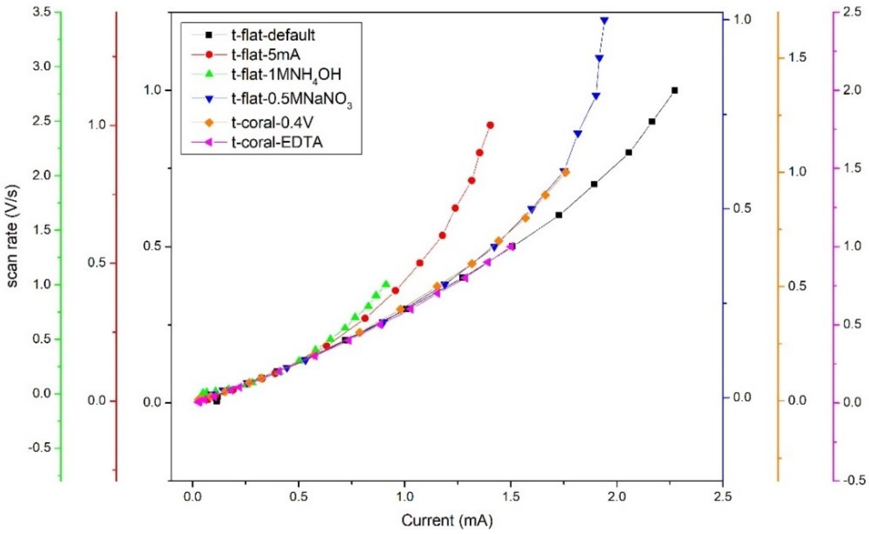


Figure S 8: plots of the scan rate vs the current determined with DLC for the six templated samples showing the different limiting currents

8. Derivation increase factor model

A model was built to simulate the roughness factor for the template-based porous Ag electrodes. The model starts with a box with sides x and y, and z. The surface on top of box A is given by

$$A = xy$$

The introduced pores are to be spherical cages with diameter d. Each cage has a surface area s of

$$s = 4\pi(0.5d)^2$$

In 2D, the packing factor of the assumed fcc structure is equal to simple cubic. Therefore, the number of cages that fit in one layer l can be described with

$$l = xy/d^2$$

The surface area for a layer of cages A_L would therefore be

$$A_L = l \cdot s$$

Using the equations above this can then be written as

$$A_L = \frac{xy}{d^2} \cdot 4\pi(0.5d)^2$$

$$A_L = xy\pi$$

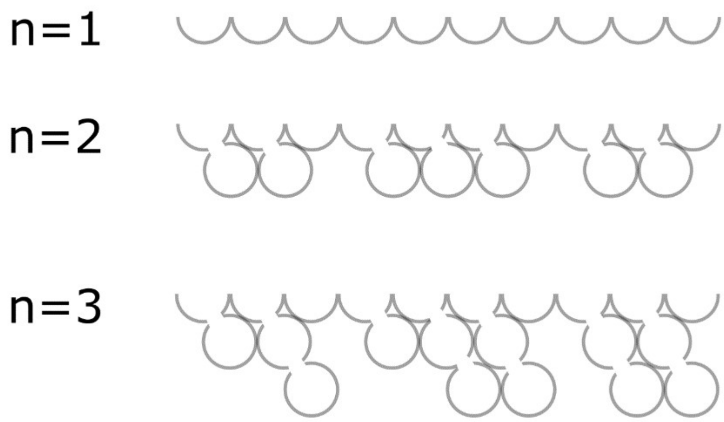


Figure S 9: Illustration of accessible pores for 1 to 3 layers. The grey line is the surface area that is included in the calculation.

For top layer 1, the layer that is exposed to the electrolyte, it is assumed that the cages are half sphere cages, as illustrated in figure S2. This ensures that the top layer is completely accessible. The surface area of layer 1 A_1 can then be described with

$A_1 = 0.5 \cdot xy\pi$

When a new layer, layer 2, is introduced, we must take two things into account. Firstly, when 2 cages touch, a window appears. This causes a loss of surface area. The model corrects for this by using a factor a . If a is 0.8, it means that each cage loses 10% of its surface area. Secondly, not all cages in the new layer are accessible. This is corrected with factor b . If 70% of the cages in layer 0 are in contact with layer one, b would be 0.7. The surface area of layer 2 A_2 will therefore be

$A_2 = abxy\pi$

For the next layer, layer 3, an extra factor b is necessary to again compensate for the loss of the new layer. The surface area of layer 3 A_3 can therefore be described by

$A_3 = ab^2xy\pi$

And so on and on, which means that the surface area of layer n A_n can be described by

$A_n = ab^{n-1}xy\pi$

The total surface area of the templated porous structure A_p will be a summation of all of these layers. For a FCC structure, the maximum amount of layers n_{max} in the box can be described by

$$n_{max} = \frac{z}{1/2\sqrt{2}d}$$

So for

$n \le n_{max}$

A_p will be

$$A_p = \left(0.5 + \sum_{k=1}^{n-1} ab^{n-1}\right) xy\pi$$

The surface area of the templated porous structure A_p will be bigger than the geometric surface area A by a factor of S

$$S = \frac{A_p}{A}$$

$$S = \left(0.5 + \sum_{k=1}^{n-1} ab^{n-1}\right)\pi$$

Finally, we want to explicitly mention that the derivation of the factor S which was discussed above is based on the following assumptions:

- The present model assumes that the pores are spherical, but the model can be adapted to other well-defined shapes.
- For the correction factors *a* (surface loss due to windows) and *b* (surface loss due to inaccessible cages) it is assumed that the effective values can be used for the whole sample.
- For the correction factor *b* it is assumed that a inaccessible cages cannot become accessible again in a next layer.
- For the increase in surface area S, it is assumed that the roughness factor is equal for both templated and non-templated electrodes.

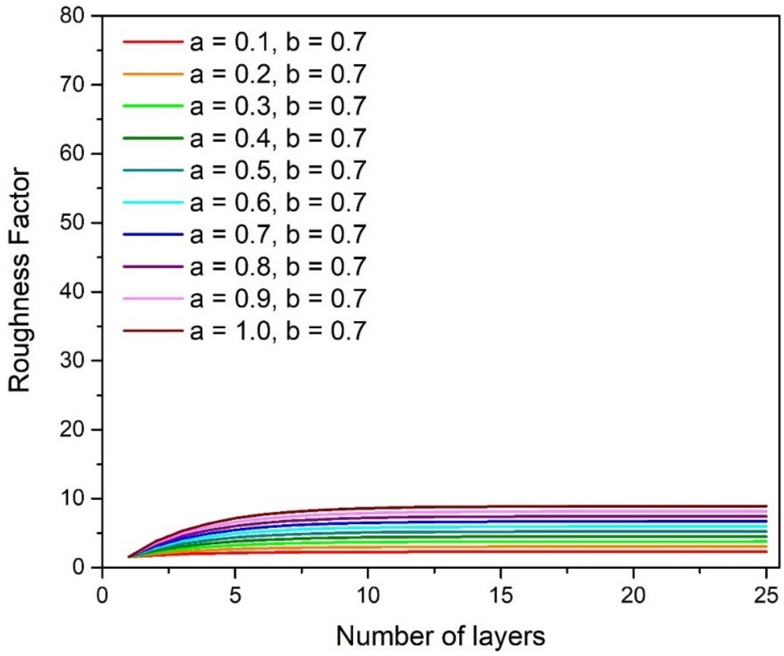


Figure S 10: Calculations of the Roughness Factor for when the parameter a is varied and b is kept constant.

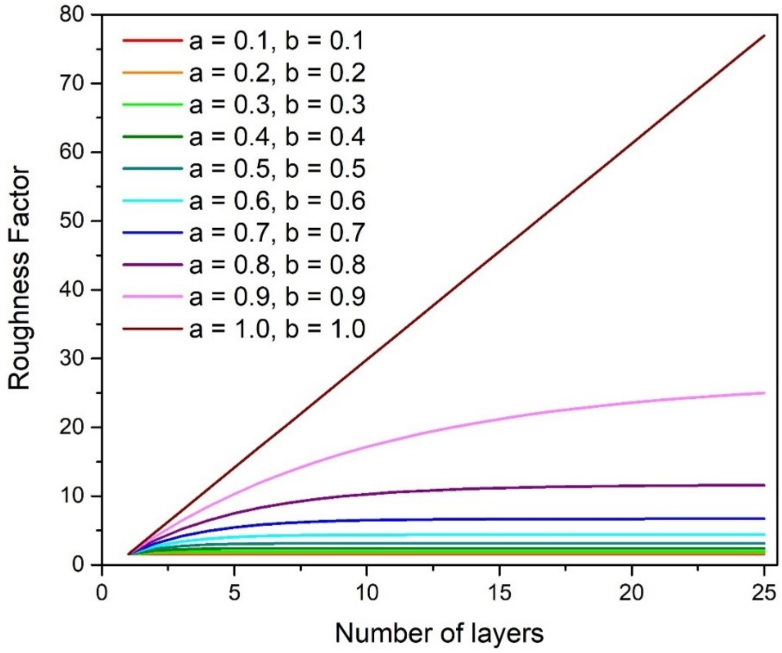


Figure S 11: Calculations of the Roughness Factor for when the parameter b is varied and a is kept constant.

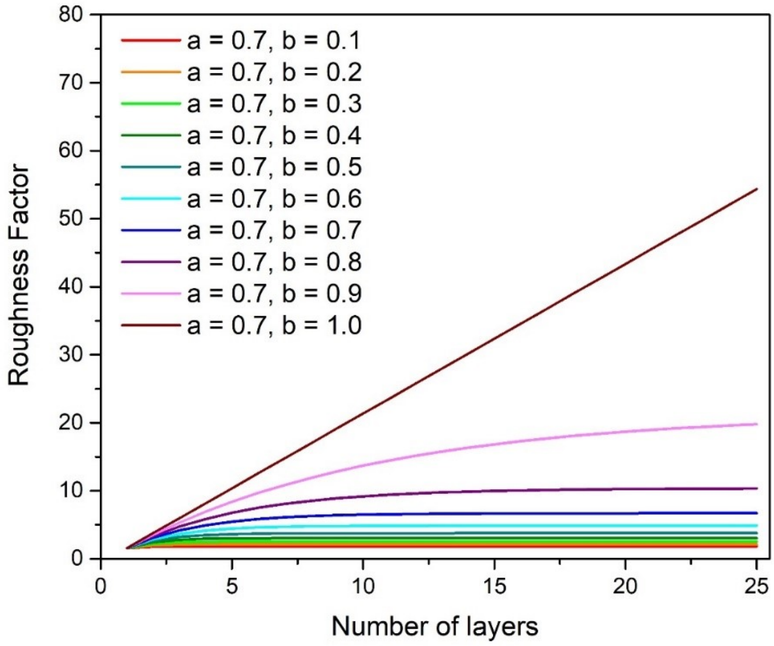


Figure S 12: Calculations of the Roughness Factor for when both the parameter a and b are varied.

9. Catalytic performance

Table S 1: Total current and partial current densities to CO and H_2 of the (non-)templated measurements at the four potentials applied during catalysis.

POROUS

<u>flat-default</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001879	-0.64	0.29635763	0.10199301	-0.7	0.002508	-0.63	0.192347795	0.01011117	-0.63	0.244352712	0.05605209
-0.9	0.004823	-0.77	0.88043002	0.12431049	-0.9	0.005412	-0.76	0.770560158	0.04261136	-0.77	0.825495086	0.08346093
-1.2	0.012071	-0.92	2.31853883	0.27705667	-1.2	0.012882	-0.91	2.395303273	0.18344553	-0.92	2.35692105	0.2302511
-1.4	0.019325	-1.04	3.74226425	0.38718409	-1.4	0.020425	-1.02	3.96646844	0.34522426	-1.03	3.854366344	0.36620417

<u>flat-5mA</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.00143	-0.65	0.23815851	0.09038235	-0.7	0.001674	-0.65	0.160694619	0.05127808	-0.65	0.199426562	0.07083022
-0.9	0.004031	-0.79	0.79635044	0.15990724	-0.9	0.004262	-0.79	0.668692118	0.1227785	-0.79	0.73252128	0.14134287
-1.2	0.011464	-0.94	2.32126954	0.27809954	-1.2	0.010998	-0.95	1.937296094	0.37050218	-0.94	2.129282816	0.32430086
-1.4	0.018459	-1.06	4.03002893	0.38238687	-1.4	0.017652	-1.07	3.277401593	0.50266963	-1.06	3.653715261	0.44252825

<u>flat-1MNH_4OH</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total} (A)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001425	-0.65	0.18452652	0.04650344	-0.7	0.001386	-0.66	0.068825092	0.0873894	-0.65	0.126675808	0.06694642
-0.9	0.00402	-0.79	0.74211983	0.06866797	-0.9	0.004193	-0.79	0.454995633	0.22316798	-0.79	0.598557731	0.14591798
-1.2	0.010582	-0.96	2.14037673	0.10443984	-1.2	0.011775	-0.93	1.614886943	0.71789312	-0.94	1.877631836	0.41116648
-1.4	0.016844	-1.09	3.45348682	0.11930972	-1.4	0.019362	-1.04	3.182054274	0.97428352	-1.06	3.317770549	0.54679662

flat-0.5M$NaNO_3$

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001912	-0.64	0.23654033	0.11201506	-0.7	0.001857	-0.64	0.15992352	0.0491114	-0.64	0.198231923	0.08056323
-0.9	0.004564	-0.78	0.73179133	0.19751685	-0.9	0.004308	-0.79	0.60014386	0.1444453	-0.78	0.665967597	0.17098108
-1.2	0.010857	-0.95	2.26697279	0.12723564	-1.2	0.011238	-0.94	1.839715053	0.42972476	-0.95	2.053343921	0.2784802
-1.4	0.017254	-1.08	3.62628291	0.15052243	-1.4	0.018258	-1.06	3.209894544	0.54022541	-1.07	3.418088727	0.34537392

coral-0MEDTA

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001758	-0.65	0.20359883	0.08480038	-0.7	0.001529	-0.65	0.118392876	0.04405582	-0.65	0.160995854	0.0644281
-0.9	0.004758	-0.78	0.83413254	0.14547229	-0.9	0.004447	-0.78	0.58950538	0.13938971	-0.78	0.71181896	0.142431
-1.2	0.012545	-0.91	2.5675507	0.27614483	-1.2	0.011869	-0.93	2.096451877	0.24844591	-0.92	2.332001288	0.26229537
-1.4	0.02007	-1.03	4.24560178	0.29452176	-1.4	0.019684	-1.04	3.87616801	0.33294641	-1.03	4.060884896	0.31373408

coral-0.4V

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001998	-0.64	0.2134403	0.07967552	-0.7	0.001525	-0.65	0.135260672	0.05488921	-0.65	0.174350485	0.06728237
-0.9	0.005333	-0.76	0.89213074	0.15455382	-0.9	0.004443	-0.78	0.71176496	0.11050065	-0.77	0.80194785	0.13252724
-1.2	0.012963	-0.90	2.48528446	0.31918875	-1.2	0.011671	-0.93	2.228432015	0.22894579	-0.92	2.356858238	0.27406727
-1.4	0.020221	-1.03	3.98742923	0.50975646	-1.4	0.019131	-1.05	3.695869762	0.37844668	-1.04	3.841649495	0.44410157

NON-POROUS

flat-default

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.000839	-0.67	0.04680776	0.10129776	-0.7	0.001045	-0.66	0.062163153	0.05561144	-0.66	0.054485457	0.0784546
-0.9	0.002533	-0.83	0.36120836	0.20495936	-0.9	0.002658	-0.82	0.421024676	0.06788929	-0.82	0.391116516	0.13642433
-1.2	0.008651	-1.00	1.40601104	0.5453532	-1.2	0.008078	-1.01	1.525604185	0.14661198	-1.00	1.46580761	0.34598259

-1.4	0.014532	-1.13	2.66532536	0.60298933	-1.4	0.013622	-1.15	2.762269185	0.2563904	-1.14	2.71379727	0.42968986

<u>flat-5mA</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001178	-0.66	0.03451493	0.17381221	-0.7	0.001215	-0.63	0.047018001	0.05127808	-0.64	0.040766463	0.11254515
-0.9	0.003195	-0.81	0.31559343	0.33371945	-0.9	0.002988	-0.78	0.352604188	0.06716706	-0.79	0.334098809	0.20044326
-1.2	0.010554	-0.96	1.56611611	0.59791401	-1.2	0.008389	-0.97	1.513828109	0.19572338	-0.96	1.539972109	0.39681869
-1.4	0.018725	-1.05	2.97136506	0.69524885	-1.4	0.013304	-1.08	2.495272705	0.30477957	-1.07	2.73331888	0.50001421

<u>flat-1MNH_4OH</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total} (A)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001002	-0.66	0.0264461	0.1310934	-0.7	0.002417	-0.63	0.012143319	0.05906208	-0.65	0.019294708	0.09507774
-0.9	0.002097	-0.84	0.30158619	0.20319827	-0.9	0.004766	-0.78	0.134833778	0.31906361	-0.81	0.218209987	0.26113094
-1.2	0.006788	-1.04	1.16681833	0.21926054	-1.2	0.010101	-0.97	0.89970023	0.80528253	-1.00	1.03325928	0.51227153
-1.4	0.010702	-1.20	2.21211441	0.21533265	-1.4	0.017049	-1.08	2.000949765	1.35329193	-1.14	2.10653209	0.78431229

<u>flat-0.5M$NaNO_3$</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001056	-0.66	0.04126614	0.07944491	-0.7	0.001015	-0.66	0.019852443	0.10472284	-0.66	0.030559291	0.09208388
-0.9	0.002886	-0.82	0.3538774	0.169001	-0.9	0.002651	-0.83	0.231135881	0.27300161	-0.82	0.292506639	0.2210013
-1.2	0.008676	-1.00	1.37257124	0.44489151	-1.2	0.008185	-1.01	1.011647478	0.74894886	-1.00	1.192109361	0.59692019
-1.4	0.013114	-1.15	2.24624239	0.46439163	-1.4	0.013146	-1.15	2.004043253	0.86017174	-1.15	2.125142821	0.66228168

<u>coral-0MEDTA</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001163	-0.66	0.08150463	0.10682463	-0.7	0.001102	-0.66	0.078944649	0.07727823	-0.66	0.08022464	0.09205143
-0.9	0.003023	-0.82	0.53775753	0.13852833	-0.9	0.003294	-0.81	0.470709022	0.26866825	-0.81	0.504233278	0.20359829
-1.2	0.008661	-1.00	1.7371686	0.18811797	-1.2	0.009155	-0.99	1.149859174	0.86089397	-0.99	1.443513886	0.52450597

-1.4	0.013718	-1.14	2.7967716	0.16448048	-1.4	0.014213	-1.13	1.919796176	1.45673081	-1.14	2.358283889	0.81060564

<u>coral-0.4V</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.001737	-0.65	0.28103852	0.05096174	-0.7	0.001792	-0.64	0.229233911	0.03466687	-0.65	0.255136217	0.04281431
-0.9	0.004828	-0.77	0.89206348	0.08280414	-0.9	0.00481	-0.77	0.896161915	0.12422295	-0.77	0.894112696	0.10351355
-1.2	0.010271	-0.96	2.09128637	0.18903816	-1.2	0.011513	-0.94	2.171903042	0.32572414	-0.95	2.131594708	0.25738115
-1.4	0.01465	-1.13	2.72930576	0.27976814	-1.4	0.018056	-1.06	3.470407289	0.68394848	-1.10	3.099856522	0.48185831

<u>Ag-foil</u>

Measurement 1					Measurement 2					Average		
RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	RHE	J_{total}	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)	E_{iR} RHE	J_{co} (mA/cm^2)	J_{H2} (mA/cm^2)
-0.7	0.000689	-0.67	0.01640491	0.05705589	-0.7	0.000622	-0.67	0.019252824	0.05633367	-0.67	0.017828868	0.05669478
-0.9	0.002289	-0.83	0.16978866	0.1935567	-0.9	0.00215	-0.84	0.219717335	0.15238979	-0.84	0.194752997	0.17297324
-1.2	0.007347	-1.03	1.00367646	0.40444683	-1.2	0.007615	-1.02	1.179887213	0.32500192	-1.03	1.091781839	0.36472437
-1.4	0.011913	-1.18	1.50473183	0.82117151	-1.4	0.01245	-1.17	1.814219463	0.84789389	-1.17	1.659475645	0.8345327

10. Electron resistance and transfer rate

Table S 2 Electron resistance and electron transfer rates for the electrodes during catalysis.

Sample	E_{iR} RHE (V)	R (Ω)	ω (Hz)	Sample	E_{iR} RHE (V)	R (Ω)	ω (Hz)
t-flat-default	-0.63	59	7	nt-flat-default	-0.66	78	33
	-0.76	21	21		-0.82	34	92
	-0.91	15	15		-1.01	11	348
	-1.02	n.a.	n.a.		-1.15	8	369
t-flat-5mA	-0.65	341	1	nt-flat-5mA	-0.63	83	28
	-0.79	26	11		-0.78	34	61
	-0.95	17	8		-0.97	12	206
	-1.07	8	31		-1.08	14	91
t-flat-1MNH$_4$OH	-0.66	128	1	nt-flat-1MNH$_4$OH	-0.63	39	110
	-0.79	27	7		-0.78	25	147
	-0.93	8	21		-0.97	12	341
	-1.04	16	8		-1.08	6	1009
t-flat-0.5MNaNO$_3$	-0.64	n.a.	n.a.	nt-flat-0.5MNaNO$_3$	-0.66	n.a.	n.a.
	-0.79	49	3		-0.83	27	194
	-0.94	42	2		-1.01	10	533
	-1.06	26	3		-1.15	8	570
t-coral-0MEDTA	-0.65	89	7	nt-coral-0MEDTA	-0.66	65	25
	-0.78	28	22		-0.81	24	79
	-0.93	11	49		-0.99	9	232
	-1.04	6	83		-1.13	6	378
t-coral-0.4V	-0.65	73	8	nt-coral-0.4V	-0.64	44	11
	-0.78	21	31		-0.77	16	38
	-0.93	11	41		-0.94	7	109
	-1.05	n.a.	n.a.		-1.06	n.a.	n.a.

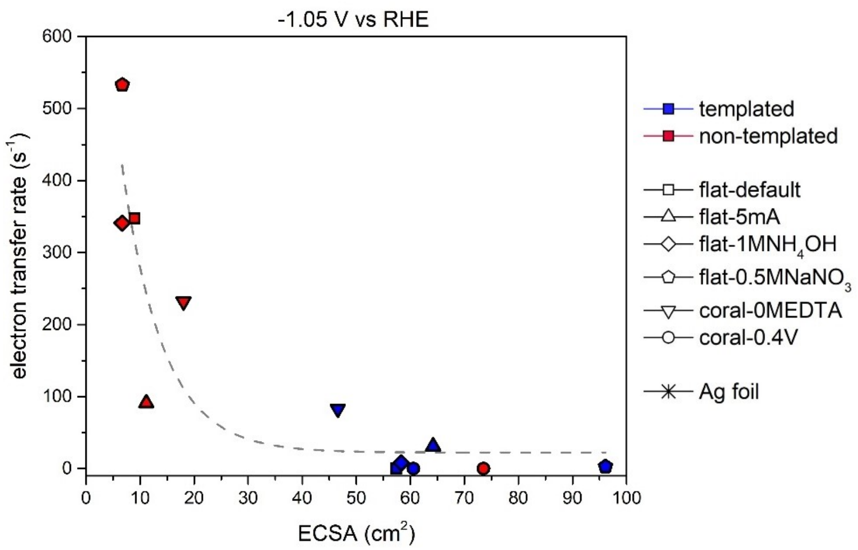


Figure S 13: Electron transfer rate for both the template-based porous (blue) and non-templated equivalent (red) samples nt-flat-default, (n)t-flat-5mA, (n)t-flat-1MNH4OH, (n)t-flat-0.5MNaNO3 and (n)t-coral-0MEDTA at -1.05 V vs RHE plotted versus the ECSA. A dashed gray line is provided as a guide for the eye.

11. Catalyst stability

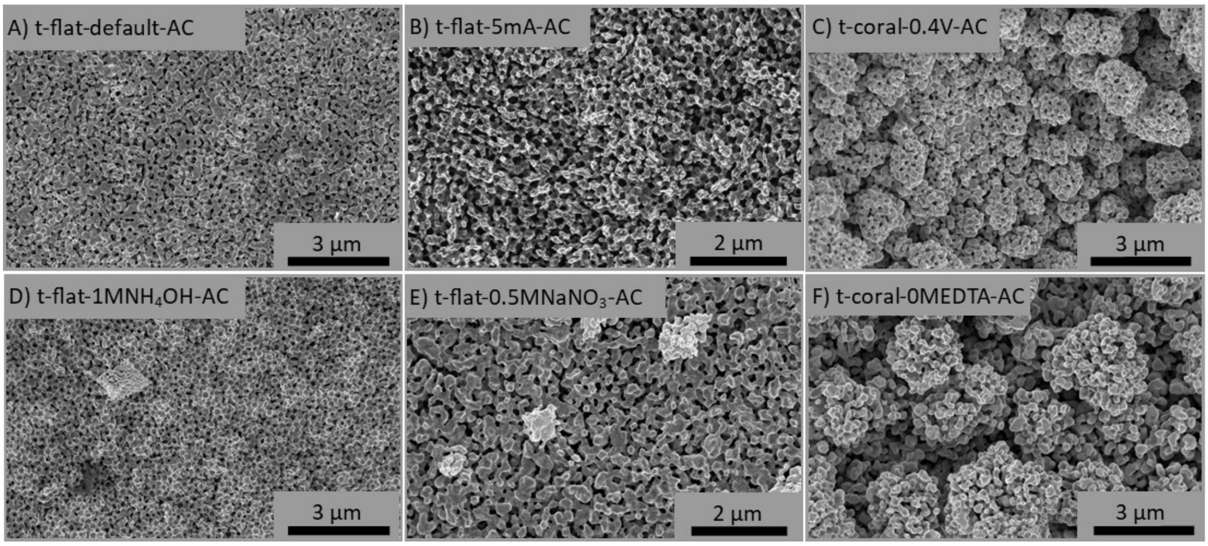


Figure S 14: SEM images of porous Ag catalysts after 1 cycle of catalysis prepared via Ag electrodeposition with slightly altered synthesis conditions: a) reference (-0.1 V vs Ag/AgCl, 0.05 M AgNO3, 1 M NaNO3, 0.01 M EDTA, 0.5 M NH4OH); b)-5mA; c) -0.4V; d) 1M NH4OH; e) 0.5M

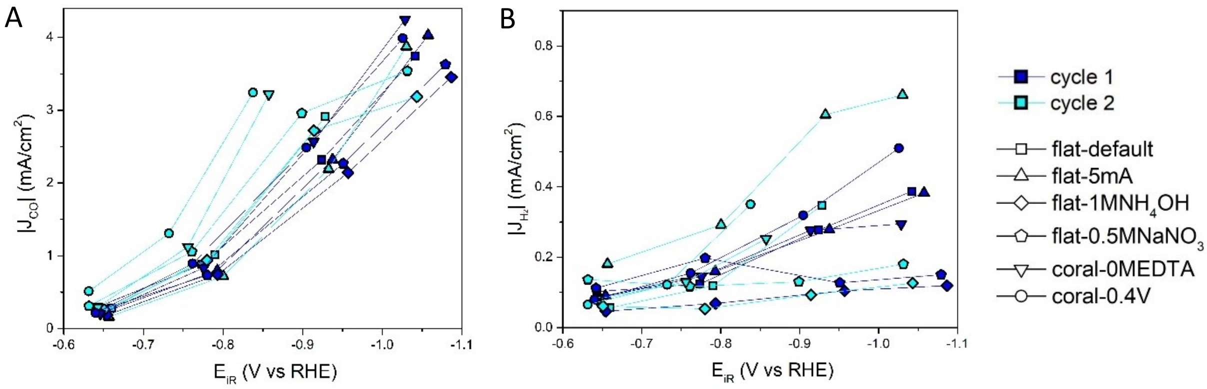


Figure S 15: partial current densities to a) CO and b) H_2 for the first and second cycle of catalysis of the electrodes t-flat-default, t-flat-5mA, t-flat-1MNH$_4$OH, t-flat-0.5MNaNO$_3$, t-coral-0MEDTA and t-coral-0.4V

12. Second cycle of catalysis