Electronic Supplementary Information (ESI)

On the role of local heating on cathode degradation during the oxygen reduction reaction in solid acid fuel cells

Maximilian Wagner[a†], Oliver Lorenz[a], Felix P. Lohmann-Richters[b], Aron Varga[a] and Bernd Abel[a]

[a]Leibniz Institute for Surface Engineering, Chemical Department, Permoserstraße 15, 04318 Leipzig, Germany
[b]Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Elektrochemische Verfahrenstechnik (IEK-14), 52425 Jülich, Germany
[c]BMW Group, Department Electrical Drive Development, Taunusstraße 41, 80807 Munich, Germany

†Corresponding author. Email: maximilian.wagner@iom-leipzig.de, Tel.: +49 341 235 3365

S1: Mass normalized current density

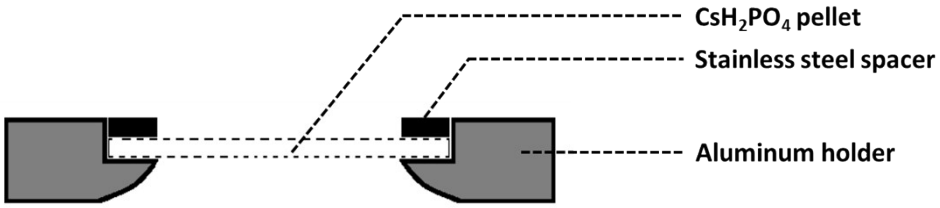
CP/**Pt@CDP$_{porous}$**-MEAs achieve current densities during cell I-V characterization of up 150 mA cm^{-2} with a platinum loading of 64 µg cm^{-2} per electrode (as published previously).[1] This results in a platinum normalized current density of about 2300 mA mg$_{Pt}^{-1}$. State of the art solid acid fuel cells with a powder electrode were reported by Papandrew et al. with maximum current densities of 1.2 A cm^{-2} during I-V characterization and a platinum loading of 1.75 mg cm^{-2}, resulting in 685 mA mg$_{Pt}^{-1}$.[2]

S2: Electrode generation using a spray drying process

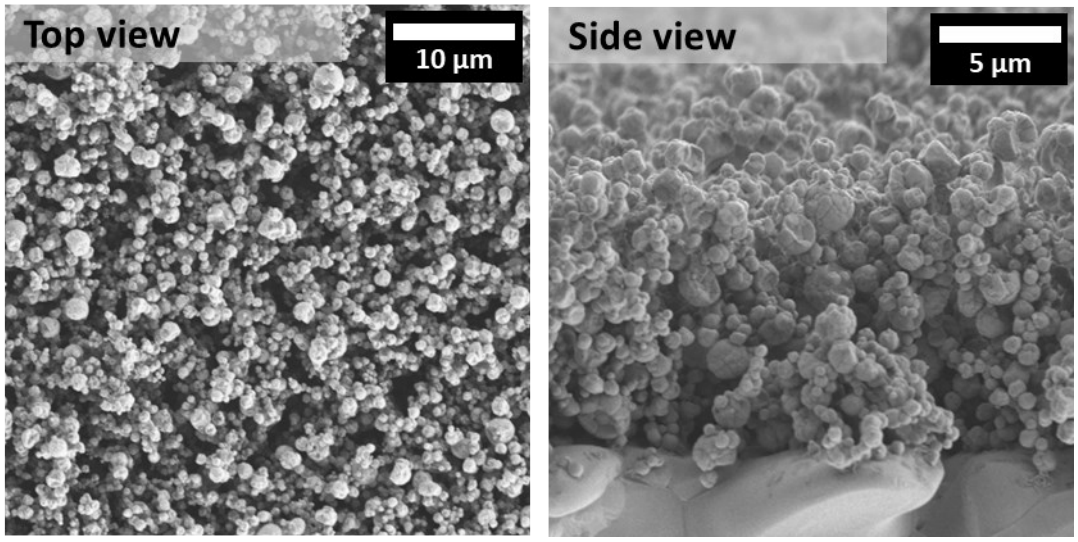
Set of spray dryer and precursor parameters used to deposit porous CsH_2PO_4 electrodes as reported previously. [1]

Precursor parameters			**Spray dryer parameters**			
CsH_2PO_4 conc.	Methanol content	PVP conc.	Temp.	Carrier gas flow rate	Precursor solution flow rate	Atomizer mesh size
10 g l^{-1}	44 wt%	0.3 g l^{-1}	303 K	80 l min^{-1}	1.5 ml min^{-1}	4 µm

Previously optimized precursor and spray parameters were used for the spray drying process.[1] To generate a 15 µm thick porous layer, a spraying time of 100 min was needed. The porous structure was applied to both sides of a CsH_2PO_4 pellet one by one. A costume made holder was used to prevent damage to the already modified side.

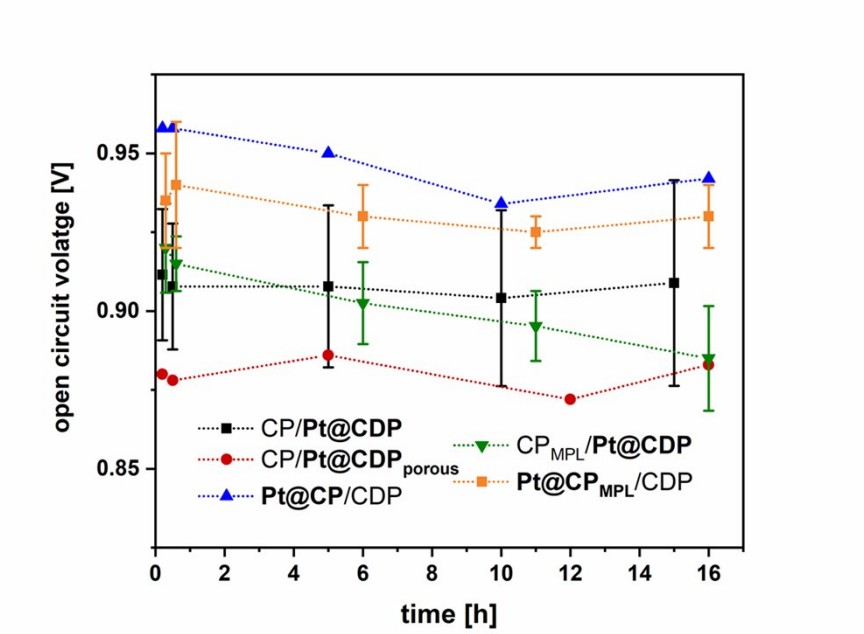


Costume made cell holder to protect the generated porous structure.



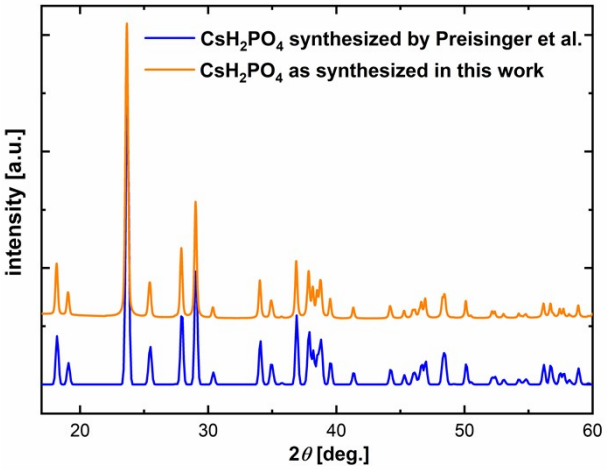
Representative SEM micrographs of the porous electrode after the spray drying process.

S3: Open circuit voltage



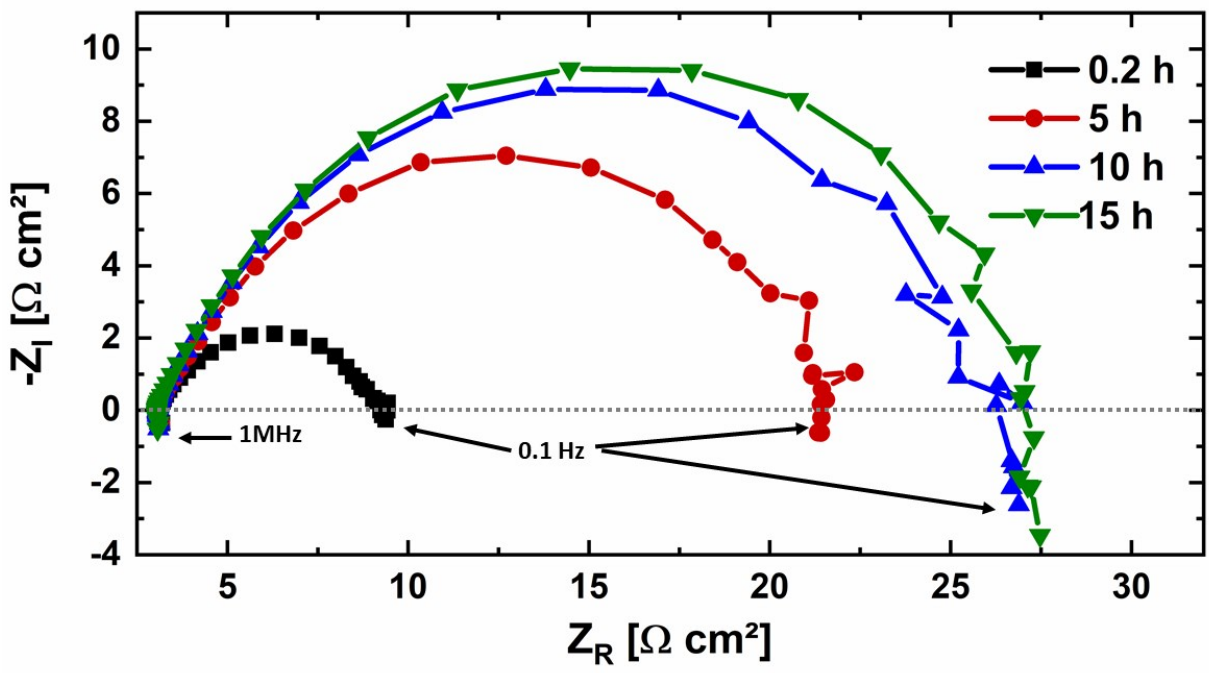
Open circuit potential for all MEA types over time. No significant change in the open circuit voltage was detected within the measurement time.

S4: X-ray diffraction experiment

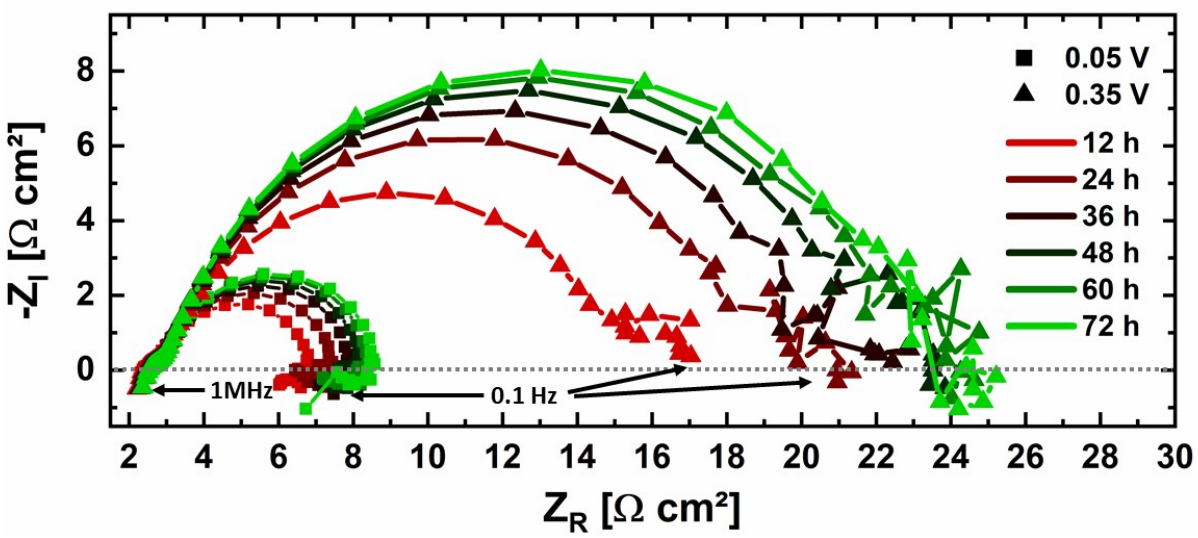


X-ray diffraction experiments to control the purity of the CsH_2PO_4 after synthesis at 25°C. A G670 Guinier Camera (Huber) using copper K_α radiation (λ = 1.541 Å) and a 2Θ-range between 15° and 70° was used. Diffractogram was compared to results of pure CsH_2PO_4 at 25°C published by Preisinger et al.[5]

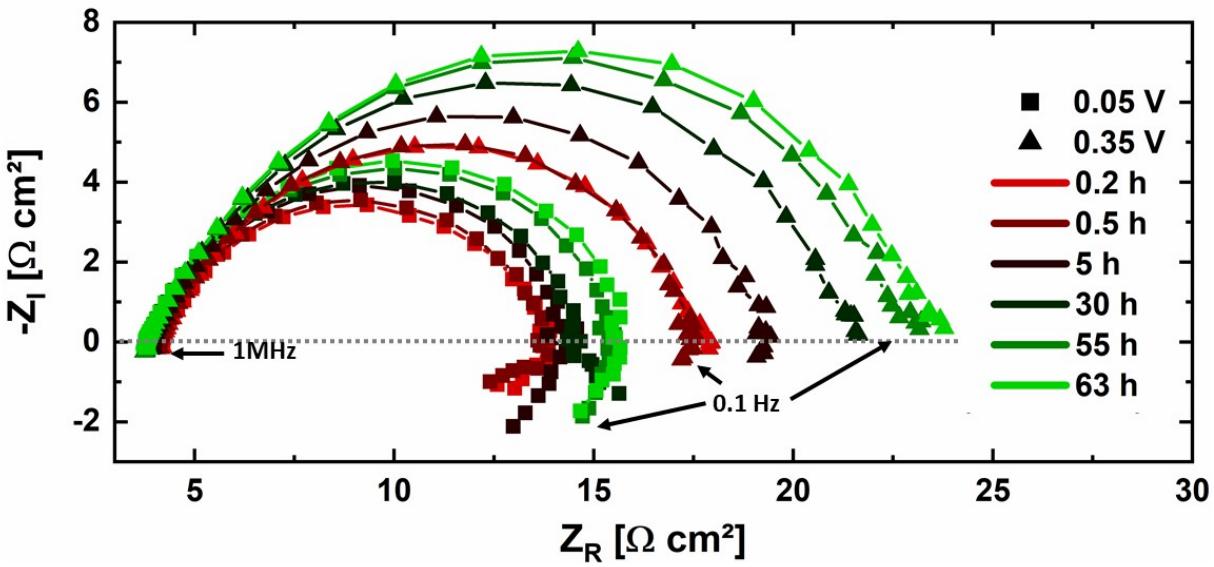
S5: Impedance measurements



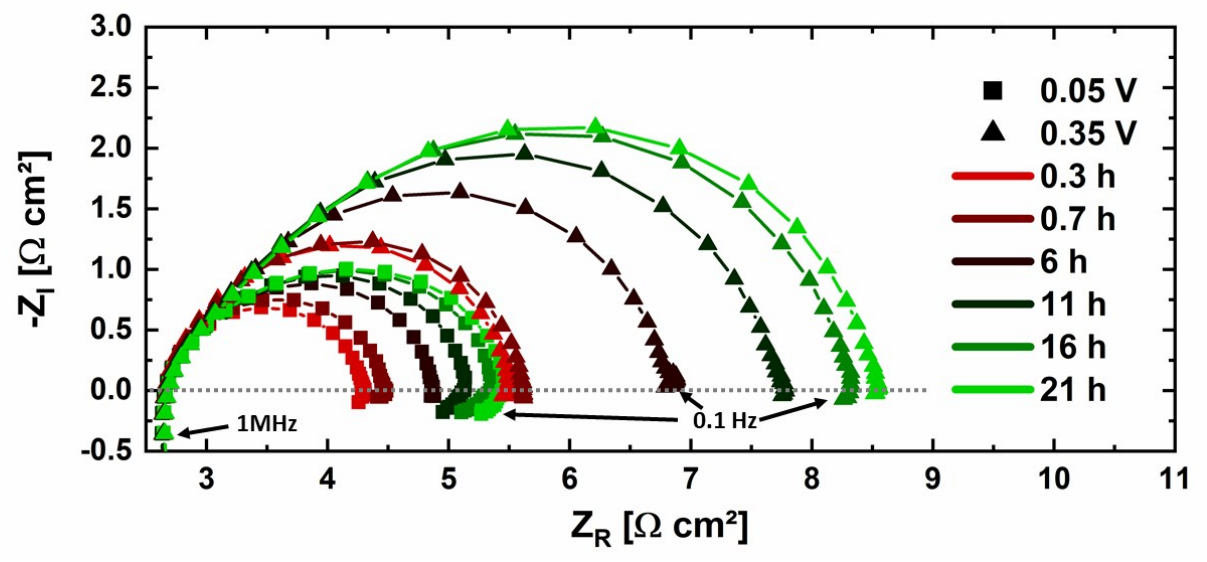
CP/**Pt@CDP**: staircase potential electrochemical impedance spectroscopy (SPEIS) after different times for voltages of 0.35 V. Voltage of 0.05 V is discussed in detail in the manuscript.



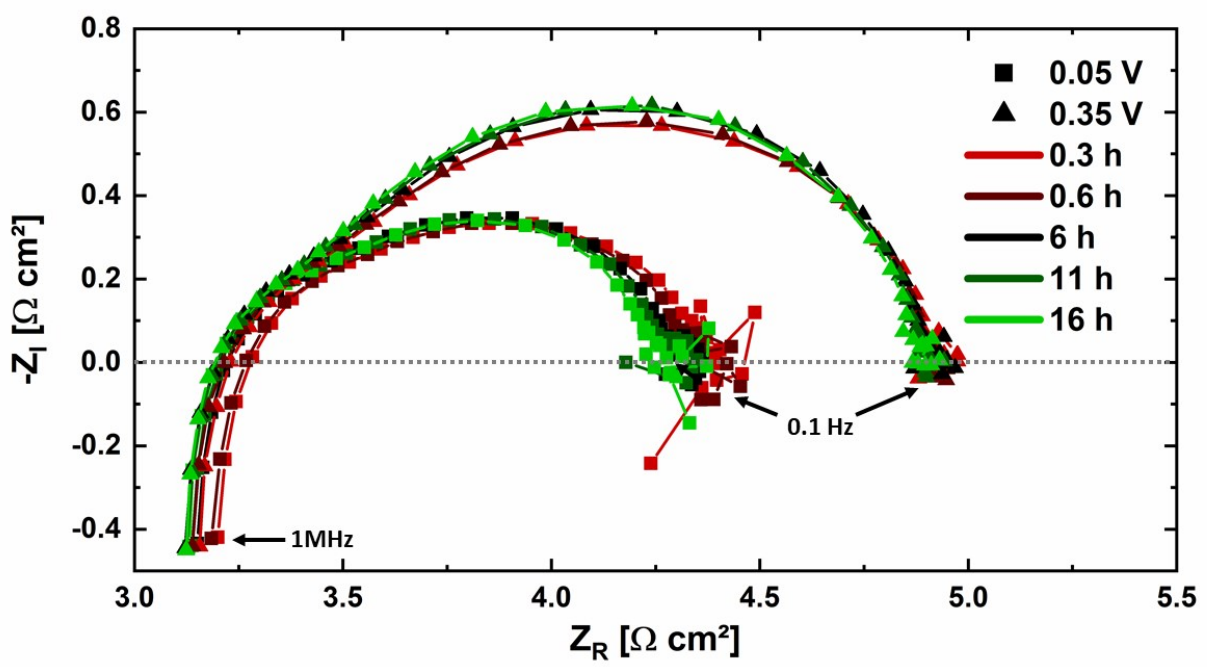
CP/**Pt@CDP** $_{porous}$: staircase potential electrochemical impedance spectroscopy (SPEIS) after different times for voltages U = 0.05 V and 0.35 V. Time is indicated by the colour and the respective voltage by the symbol.



Pt@CP/CDP: staircase potential electrochemical impedance spectroscopy (SPEIS) after different times for voltages U = 0.05 V and 0.35 V. Time is indicated by the colour and the respective voltage by the symbol.

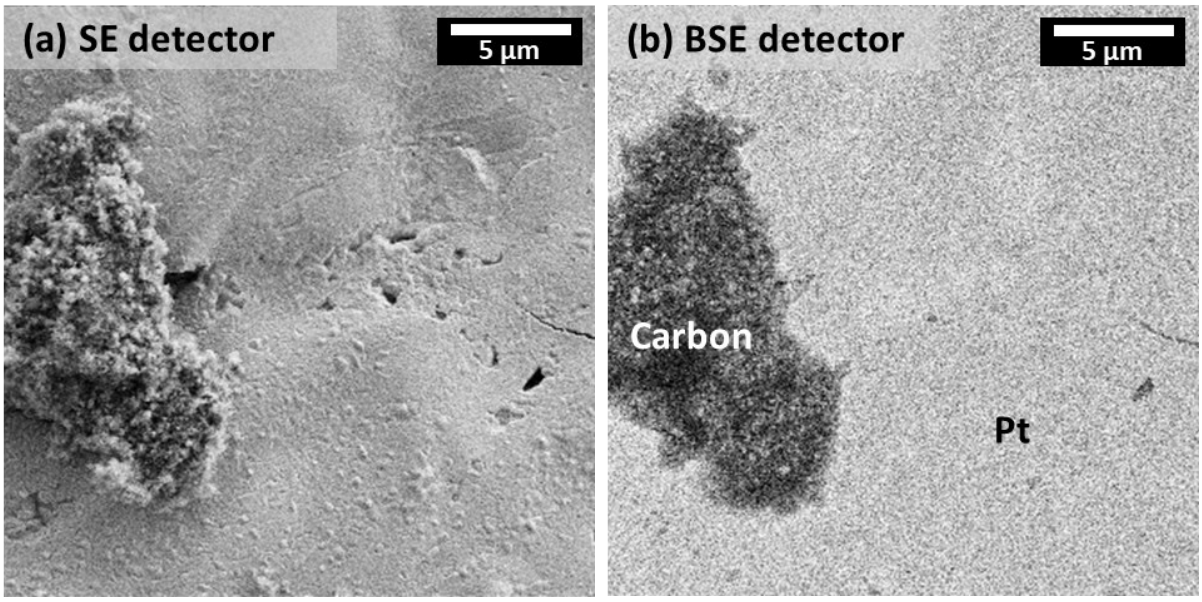


Pt@CP$_{MPL}$/CDP-MEA: staircase potential electrochemical impedance spectroscopy (SPEIS) after different times for voltages U = 0.05 V and 0.35 V. Time is indicated by the colour and the respective voltage by the symbol.

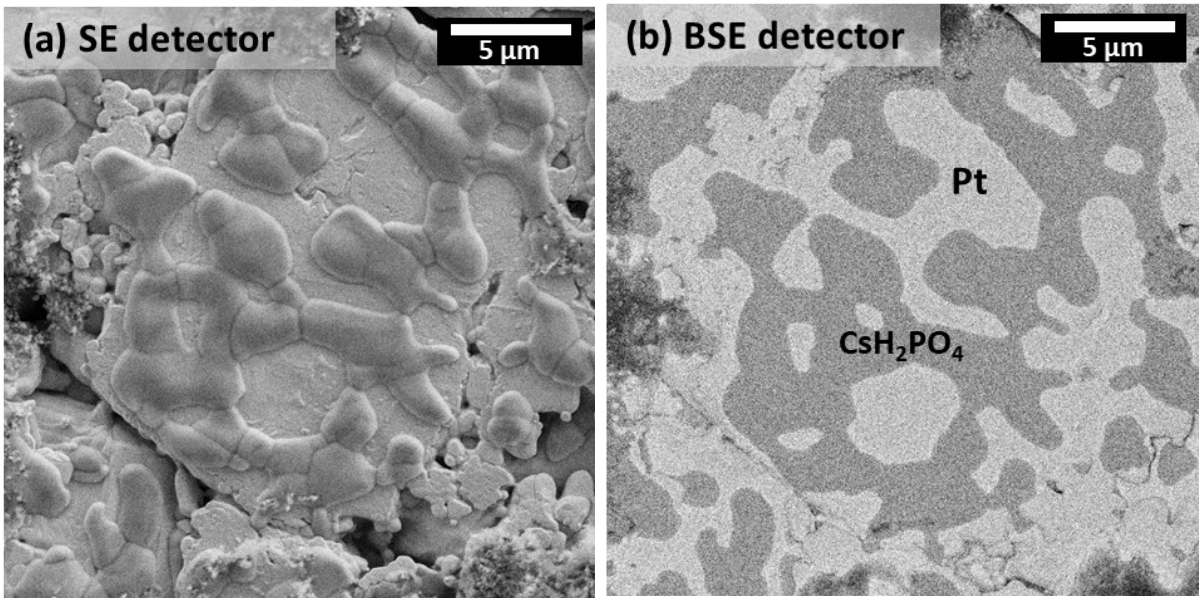


CP$_{MPL}$/**Pt@CDP**: staircase potential electrochemical impedance spectroscopy (SPEIS) after different times for voltages U = 0.05 V and 0.35 V. Time is indicated by the colour and the respective voltage by the symbol.

S6: SEM analyzation of CP_{MPL}/Pt @CDP

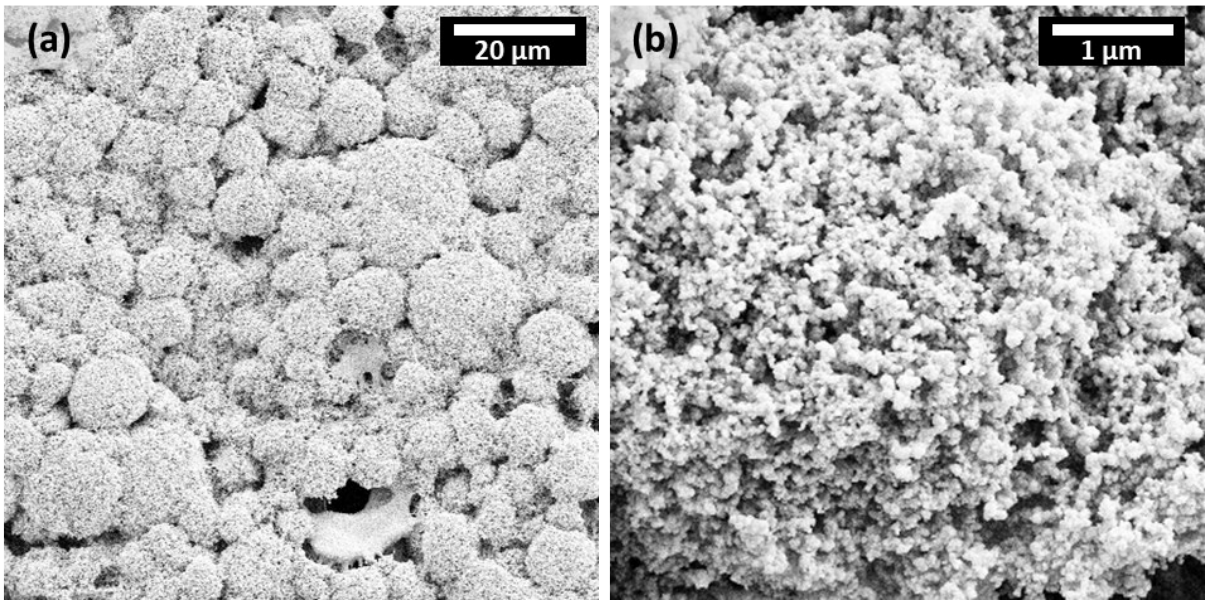


SEM micrographs of the CP_{MPL}/**Pt@CDP** anode after carbon paper removal. (a) Secondary electron (SE) detector. (b) Back scattering electron (BSE) detector. Relevant phases are marked in (b).



SEM micrographs of the CP_{MPL}/**Pt@CDP** cathode after carbon paper removal. (a) Secondary electron (SE) detector. (b) Back scattering electron (BSE) detector. Relevant phases are marked in (b).

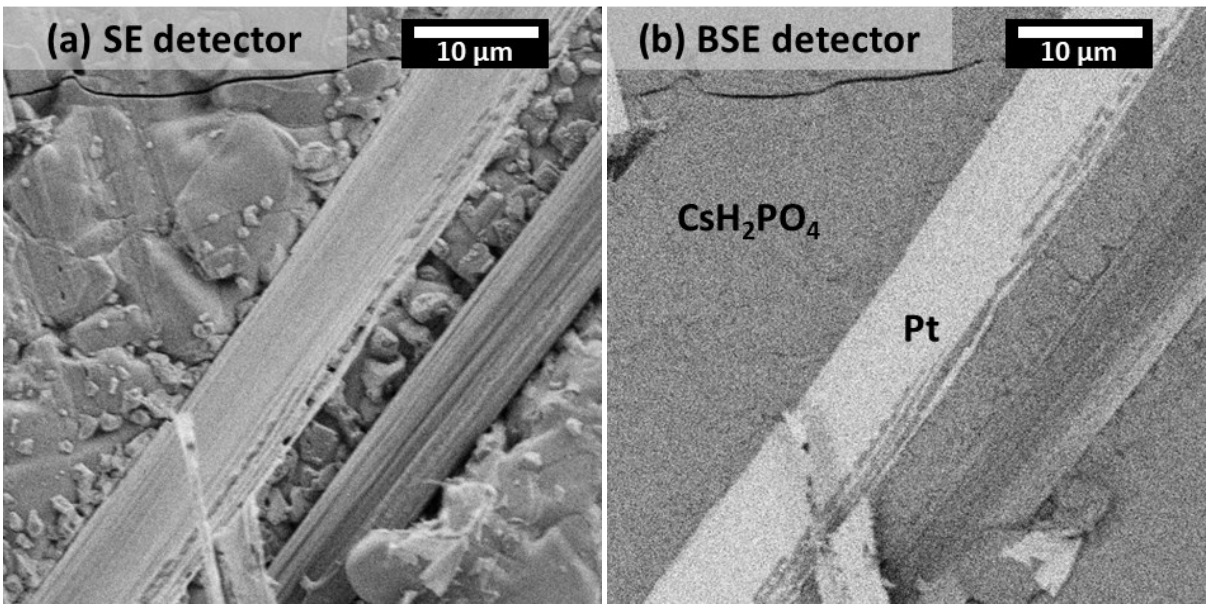
S7: SEM analyzation Pt@CP_{MPL}/CDP



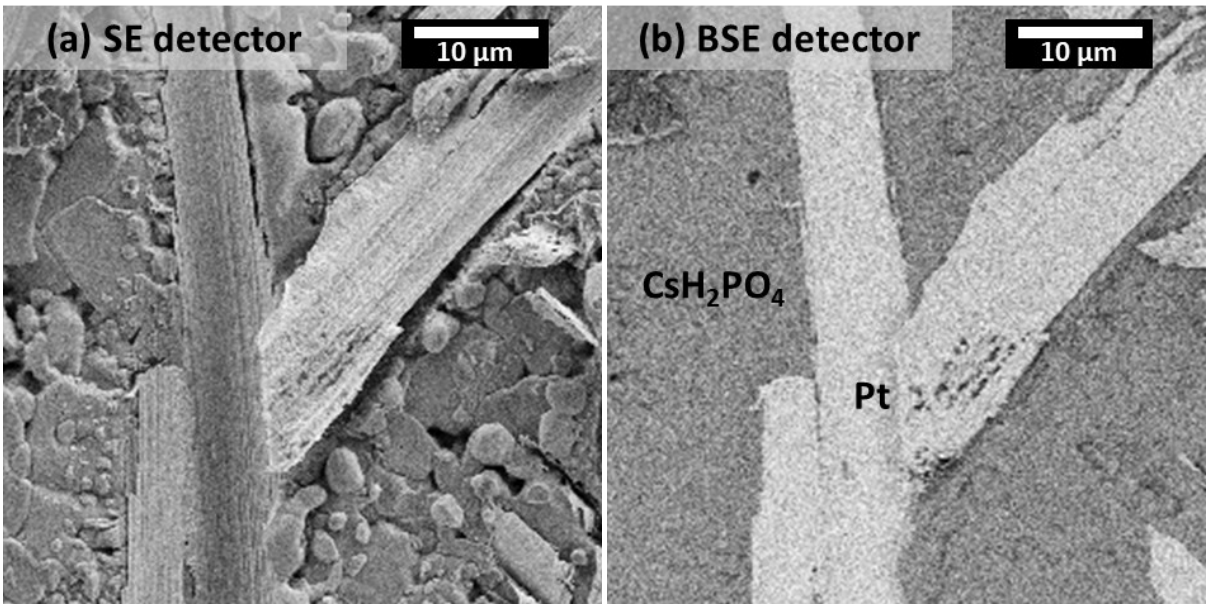
SEM micrographs of the CP_{MPL} after platinum deposition.

S8: SEM analyzation Pt@CP/CDP

Two different sections of the **Pt@CP**/CDP cathode surface were analyzed by SEM. During removement of the carbon paper, platinum occasionally detachment from the carbon fiber leaving behind a platinum coated imprint. Morphological changes of the electrolyte close to the imprint are visible.



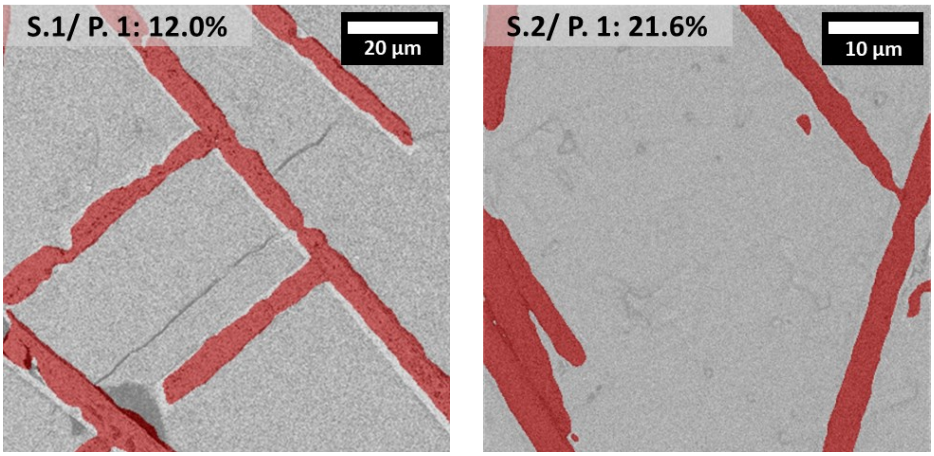
SEM micrographs of the **Pt@CP/**CDP cathode after carbon paper removal. (a) Secondary electron (SE) detector. (b) Back scattering electron (BSE) detector. Relevant phases are marked in (b).



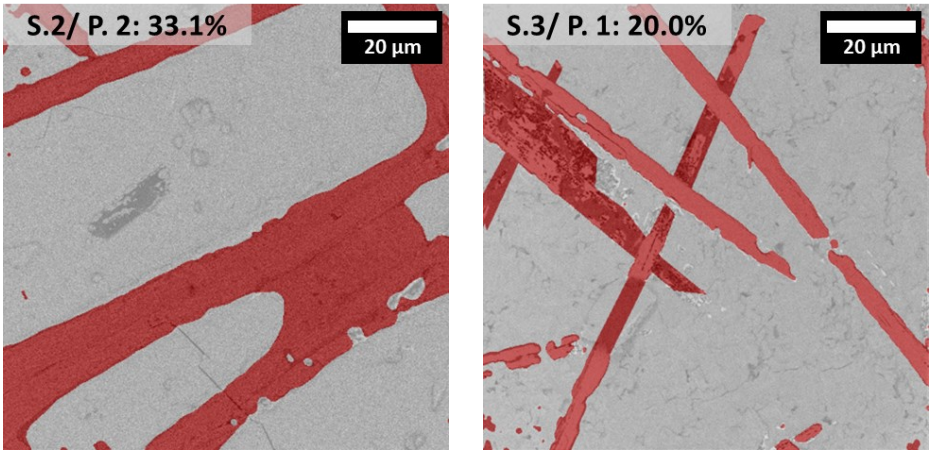
SEM micrographs of the **Pt@CP/**CDP cathode after carbon paper removal. (a) Secondary electron (SE) detector. (b) Back scattering electron (BSE) detector. Relevant phases are marked in (b).

S9: Contact area CsH_2PO_4 – Platinum

After measuring platinum plated carbon paper (CP) electrodes, the carbon paper was removed prior to scanning electron microscope (SEM) investigation. At areas where carbon strands were in contact with the CsH_2PO_4 surface, imprints can be seen on the surface. During the removal process, platinum detached from the carbon fibers and is present at the electrolyte surface. Using a back-scattering detector, a high material contrast could be achieved for magnifications between 500 and 1000 depending on the sample, making an image processing with the image J software (Version 1.52t) possible. Representative overlays of the SEM micrographs and contact area determined by the image processing are shown. There is a large variation between the samples, resulting in a relatively large standard deviation. Since this analysis was designed to provide a rough overview of the area coverage the scale of 7 measurements was considered sufficient by the authors.



Representative overlays of the SEM micrographs and contact area determined by the image processing for sample 1, position 1 (S.1/P.1) and sample 2, position 1 (S.2/P.1).



Representative overlays of the SEM micrographs and contact area determined by the image processing for sample 2, position 2 (S.2/P.2) and sample 3, position 1 (S.3/P.1).

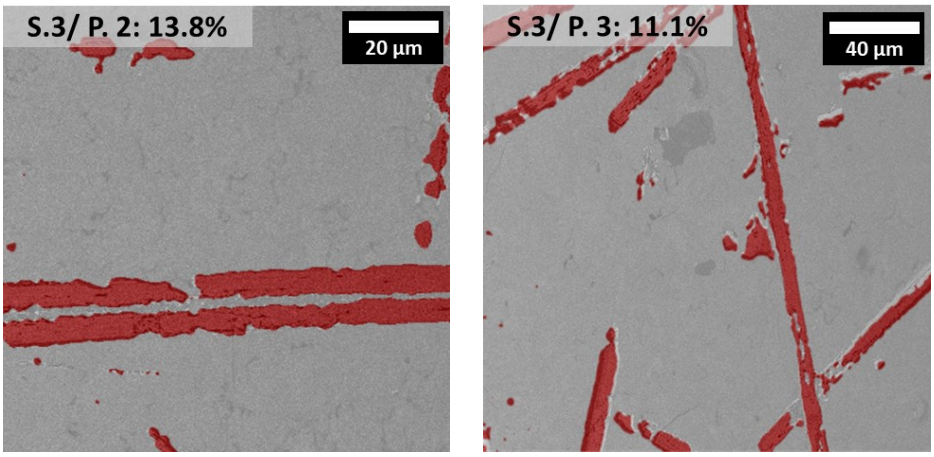


Figure S 3 Representative overlays of the SEM micrographs and contact area determined by the image processing for sample 3, position 2 (S.3/P.2) and sample 3, position 3 (S.3/P.3).

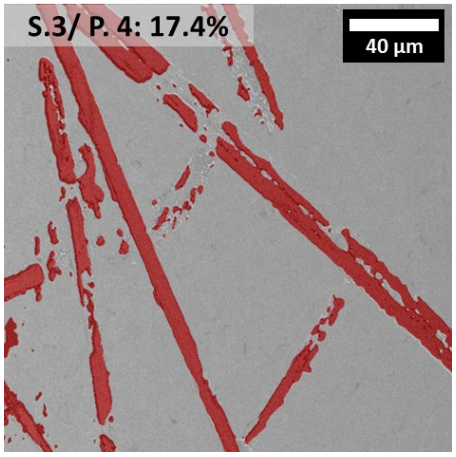


Figure S 4 Representative overlays of the SEM micrographs and contact area determined by the image processing for sample 3, position 4 (S.3/P.4).

Results of analyzing a total of 7 different locations on 3 different cells are summarized in the table. Overall, an area coverage of 18 ± 9% was obtained. Which represents a considerable decrease of the platinum coverage compared to the completely covered platinum thin film electrodes.

Results of analyzing a total of 7 different locations on 3 different cells. An overall coverage of 18 ± 9% was obtained.

Sample	Position	Area coverage [%]
1	1	12.0
2	1	21.6
2	2	33.1
3	1	20.0
3	2	13.8
3	3	11.1
3	4	17.4

S10: Calculation of the sheet resistance

At 20°C, platinum bulk metal has an electrical resistivity of $1.05*10^{-7}$ Ω m. With a thickness of 30 nm, the electrical resistivity of the platinum thin film can be described in good approximation with bulk behavior.[3] With a temperature coefficient "α" of 0,003927 K^{-1} and ΔT = 220°C, the resulting electrical resistivity "ρ" at operating temperature of 240°C can be calculated by: [4]

$$\rho_{240°C} = \rho_{20°C} * (1 + \alpha\Delta T) = 1{,}05 * 10^{-7} * (1 + 0{,}86394)\Omega m = 1.98 * 10^{-7}\,\Omega m$$

The resulting sheet resistance for a layer thickness of t = 30 nm can be calculated by:

$$R_{S,240°C} = \frac{\rho_{240°C}}{t} = \frac{1.98 * 10^{-7}\,\Omega m}{3.0 * 10^{-8}\,m} = 6.6\,\Omega$$

References

[1] Wagner, M.; Dreßler, C.; Lohmann-Richters, F. P.; Hanus, K.; Sebastiani, D.; Varga, A.; Abel, B., *J. Mater. Chem. A*, (2019) **7**, 27367.

[2] Papandrew, A. B.; Chisholm, C. R.I.; Elgammal, R. A.; Özer, M. M.; Zecevic, S. K., *Chem. Mater.*, (2011) **23**, 1659.

[3] Avrekh, M.; Monteiro, O.R.; Brown, I.G., *Applied Surface Science*, (2000) **158**, 217.

[4] Serway, R. A., *Principles of physics*, (1998-), Fort Worth, Saunders College Pub.

[5] Preisinger, A.; Mereiter, K.; Bronowska, W., *MSF*, (1994) **166-169**, 511.