Supplementary Information for

Engineering macroporous carbon film support for freestanding Fe-N-C cathode at high current densities

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1. Experimental section

1.0. Chemicals

Styrene (ReagentPlus[®], with 4-tert-butylcatechol as stabilizer, \ge 99%), potassium persulftate (\ge 99%), 1-butanol (99.9%), 1,3-propanediol (98%) and LUDOX[®] CL colloidal silica (30 wt% suspension in H₂O) were obtained from Sigma-Aldrich. Polyvinyl alcohol (87-89% hydrolyzed, low molecular weight) was purchased at VWR. Mesophase pitch (MP) was obtained from Bonding Chemical USA.

1.1. Synthesis of the polystyrene nanospheres

Styrene was washed two times with 0.5 M sodium hydroxide solution (1:1 vol/vol ratio of NaOH solution : styrene) and subsequently one time with distilled water (1:1 vol/vol ratio) to remove polymerization inhibitors. The purified styrene was added to 180 mL of Argon-degassed DI water at 80°C, prior to the dropwise addition of 20 mL (0.08 g) Argon-degassed potassium persulfate aqueous solution during 300 rpm agitation. After 22 h, the colour of the solution turned white due to the formation of polystyrene colloidal nanospheres, which were recovered by centrifugation at 10000 rpm for 10 minutes. After a two further centrifugation steps with water exchange between the steps, the resulting powder was dried at 80°C for 12

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hours and finally ground into a fine powder in a mortar and pestle for use as a macroporedirecting hard template.



Scheme S1: a) Representative molecular structure of mesophase pitch and PVA. b) Preparation sequence of the macroporous carbon film.

1.2. Synthesis of the macroporous carbon film

a) Slurry preparation

0.1 g mesophase pitch and 0.25 mL n-butanol are ball milled (TOB-YXQM-4L, 600 rpm, 5 min forward, 5 min backward, 5 min waiting, total time of active milling: 2 hours) using 20 g of zirconia balls (diameter: 3 mm) in a zirconia jar (volume: 50 mL). 0.5 g polyvinyl alcohol (PVA, 86-89% hydrolyzed, low molecular weight) and polystyrene nanospheres (PS, 0 g/ 0.25 g/ 0.63 g/ 1.05 g / 1.25 g / 1.64 g) are ultraprobesonicated (Fisherbrand) in 5 mL DI water for 10 minutes (5 seconds – 5 seconds break). Then the PVA/PS suspension is added to the mesophase pitch in the ball mill jar, and ball milled (TOB-YXQM-4L, 600 rpm, 5 min forward, 5 min backward, 5 min waiting, total time of active milling: 3 hours). For the last 30 minutes of active ball milling time 0.47 mL 1,3-propanediol (PD) is added to the jar. The slurry and the

balls are poured into a centrifuge tube with a 2 mm hole at the bottom, to separate the slurry from the balls. The slurry drops are collected in a vial below the centrifuge tube.

b) Macroporous carbon film preparation

The slurry was cast on the backside of the BLODLÖNN mirror (IKEA) using a doctor blade with a 500 μ m and 1000 μ m gap between doctor blade and substrate. Subsequently, the film is dried for 12 hours. Then, the films are peeled of, cut into 2 cm x 4 cm pieces, and stored in plastic petri dishes in nitrogen atmosphere for the next steps. The films are sandwiched between two carbon papers (H23, Freudenberg), which are themselves sandwiched between two carbon felts for the oxidative stabilization step. (MTI OTF-1200X , Compressed Air, Flowrate: 0.5 L/min, RT – Heating Rate: 10°C/min – Temperature Target: 130°C – Heating rate: 0.2°C/min – Temperature Target: 210°C – Dwell Time: 600 min – Temperature after Dwell Time 210°C). The stabilized films are transferred into vials with toluene for 30 minutes. This extraction protocol was repeated four times to achieve complete removal of the polystyrene hard template. Then the films are sandwiched again in the same sandwich layer combination as for the oxidative stabilization and carbonized. (MTI OTF-1200X, Nitrogen, Flowrate: 0.5 L/min, RT – Heating Rate 1°C/min – Temperature Target: 200°C – Heating rate: 0.1 / 0.5 / 1.0 °C/min – Temperature Target: 900°C – Dwell Time: 30 min).

1.3. Physical Characterization

a) Nitrogen sorption

Initially, the carbon materials (20 mg) are degassed at 220°C for 16 hours with Smart VacPrep (Micromeritics). Nitrogen sorption experiments on the carbon materials were conducted on a TriStar II PLUS (Micromeritics) adsorption analyzer at 77 K within a relative pressure range from 10^{-5} to 0.99 p/p₀. The BET surface area was obtained with the BET equation, where the fitting region was determined by the Rouquerol method in the TriStar software. The pore size distribution up to a pore diameter of 50 nm was calculated using slit geometry and heterogeneous surface-2D-NLDFT model in-built with the TriStar software.

b) Mercury intrusion porosimetry (MIP)

Macropores in carbon materials and catalyst layers can be resolved with mercury intrusion porosimetry (MIP). MIP measurements were performed using an AutoPore IV Servies (Micromeritics) in the pressure range of $2.5 \cdot 10^{-2}$ to $2.28 \cdot 10^{3}$ bar. The cumulative mercury intrusion volume can be translate to a cumulative pore volume as a function of the pore diameter using the analusis software AutoPore IV (version 9500).

c) Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a Perkin-Elmer TGA8000. The samples were heated in a nitrogen atmosphere with a heating rate of 1°C/min from 30°C to 1000°C in case of the film components. The carbon burn-off for the SiO2 templated films was carried out in compressed air with a heating rate of 10°C/min and a constant temperature holding step at 900°C for 10 minutes.

d) Dynamic light scattering (DLS)

The size of the synthesized polystyrene particles is measured with DLS in a Malvern Zetasizer MicroV. The samples are dispersed for 10 minutes in a ultrasonicated bath. The program carried out 60 runs for 10s each and is repeated three times.

e) Scanning electron microscopy (SEM)

The morphology of the carbon films is imaged with a Zeiss Leo Gemini 1525. The samples are attached with double-sided carbon tape on the aluminum stub for top or cross-section imaging. Then a film of chromium (40 nm) is sputtered onto the samples before loading into the vacuum chamber.

f) X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed with a Thermo Fisher K-Alpha XPS system to probe the elemental surface composition of the supports and catalysts. The spectra were measured at pressures below $5 \cdot 10^{-8}$ bar with a monochromatic Al-K_a excitation source, and analysed using Avantage software. The C1s peak at 284.8 eV was used for spectrometer calibration.

g) Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

The Fe content of the catalysts was measured with ICP-MS. The samples (5 mg) were digested in aqua regia 25 v/v% HNO₃ (70%, Certified AR, Eur. Ph., for analysis Fisher Chemical, Fisher Scientific and 75 v/v% HCl (37%, Certified AR, Eur. Ph., for analysis Fisher Chemical, Fisher Scientific) using a MARS 6 microwave system at 215°C for 15 minutes. The solutions were further filtered (0.22 μ m) and diluted with 2% HNO₃ to prepare samples with Fe concentrations below 500 ppb. The diluted samples were submitted to the Agilent 7900 ICP-MS spectrometer referring to the internal scandium standard and calibration solutions with Fe concentrations of 0, 5, 50, 100, 200 and 500 ppb. Two measurements were taken for each sample to demonstrate accuracy and reproducibility.

h) Resistivity measurements

The conductivity of the film at different stages in the preparation protocol was calculated from the resistivity by a four-probe-measurement along the measured thickness obtained.

i) Thermomechanical analysis (TMA)

Thermomechanical analysis of the mesophase pitch precursor was performed in a HITACHI TMA6300 with an applied force of 49 mN. During analysis, the sample was exposed to a heating rate of 1°C/min with a temperature target of 800°C.

1.4. Electrochemical characterization with the rotating disc electrode (RDE)

Electrochemical characterization was performed in a standard three-electrode cell using a potentiostat Multi AUTOLAB/M101 (Metrohm). The working electrode was a glassy carbon disk ($\emptyset = 5$ mm). The carbonized macroporous film supports (20 mg) were ball milled in a zirconia jar with zirconia balls ($\emptyset = 3$ mm) for 3 hours at 300 rpm with 2 mL isopropanol. The ball-milled powders / Vulcan XC 72 supports (15 mg) were functionalized with iron(II) phthalocyanine (99%) (1.7 mg for 1 wt% Fe loading) in 20 mL isopropanol in a centrifuge on a shaker for 12 hours. After evaporation of the solvent at 80°C, the dried catalysts can be characterized. Inks contained 4 mg of the catalyst, 240 µg isopropanol (99.5%, Sigma Aldrich), 720 µg 18.2 MΩ deionized water and 40 µg of ionomer dispersion NafionTM D-521. After sonication in ice bath for 30 minutes, the ink is dropcasted (10 µL) on a freshly polished circular area glassy carbon disk to load 200 µg_{Cat}/cm². The ink was dried under rotation (300 rpm). A

glassy carbon rod served as counter electrode. A Hg/HgO (30 mm, Redox.me) reference electrode was calibrated against a H₂ (1 bar) purged Pt RDE tip (Ø = 3 mm, Metrohm) working electrode (1000 rpm) and platinum wire counter electrode in 0.1 M KOH (99.995% Suprapur). After purging N₂ (99.9998%, Ultrapure Plus), 50 cyclic voltammograms were recorded at 50 mV/s and 1600 rpm in the potential range of 0.20 V_{RHE} to 1.05 V_{RHE} to precondition the catalyst. Subsequently, 3 cyclic voltrammgramms were recored at 10 mV/s and 0 rpm in the potential range of 0.20 V_{RHE} to 1.10 V_{RHE} to evaluate the capacitive current. After purging O₂ (99.99998% BIP* Plus) for 15 minutes, three cyclic voltammograms at 10 mV/s and 1600 rpm were recorded in the potential range from 0.25 V_{RHE} to 1.10 V_{RHE}. The pseudocapacitance was corrected by subtracting the current obtained previously in N₂ from the cyclic voltammograms in O₂. The ohmic drop was calculated for each measurement by means of electrochemical impedance measurements from 10⁵ to 10⁻¹ Hz at 0.85 V at 1600 rpm by taking the first intercept of the real impedance axis in the Nyquist plot.

The kinetic current densities (j_{kin}) were calculated at 0.85 V_{RHE} using the geometric disk current density (j_d) at 0.85 V_{RHE} and the limiting current density (j_{lim}) at 0.25 V_{RHE} following equation (1):

$$j_{kin} = \frac{j_d \cdot j_{lim}}{j_d - j_{lim}} \tag{1}$$

The mass activity (MA) can be calculated with the following equation (2):

$$MA = \frac{J_{kin}}{Catalyst \ Loading}$$
(2)

1.5. Electrochemical characterization with the Gas-Diffusion-Electrode (GDE) half-cell setup

Electrochemical characterization was performed in a updated small gas-diffusion-electrode¹ (GDE) cell using a potentiostat PGSTAT204 with FRA32M Module (Metrohm) in combination with a BOOSTER10A. The macroporous carbon film supports are functionalized with FePc in isopropanol with solvent evaporation and subsequent washing step in water. Before testing in the GDE the samples are lasercut to circular electrodes. (\emptyset = 3 mm) A weight of Sustainion XA-9 ionomer corresponding to half of the electrode weight is dropcasted onto macroporous carbon electrodes. (33 wt%/66wt% I/C). Inks formulations of 5mg FePc/Vulcan XC 72, 65 μL Sustainion (5 wt%) and 6.25 mL ethanol are subjected to sonication in an ice bath for 1 hour. Then, the inks were sprayed manually with an airbrush set (Paasche) powered by an Iwata Smart Jet Pro Airbrush compressor on a Freudenberg H23C8 GDL while heated at 60°C on a heating plate. The gas diffusion layer is weighed pre and post-cathode spraying to determine the cathode catalyst loading. For the working electrode preparation, either the FePc/macroporous film/ Sustainion electrode is placed on top of a H23C8 GDL, or a piece (ϕ = 3 mm, Boehm) is cut out of the FePc/Vulcan XC 72/GDE, and inserted into a hole (ϕ = 3 mm, Boehm) of a H23C8 GDL (Freudenberg). A Sustainion X37-50 Grade 60 membrane (\emptyset = 20 mm) is positioned between the upper cell body and the H23C8 GDL with its hydrophobic coating facing the AEM and with the GDE catalyst layer facing the membrane exactly located underneath the hole in the upper cell body. The lower cell body with a flow-field facing towards the H23C8 GDL is connected to a bubbler and gas flow meter (Bronkhorst) with a flow rate of 300 mL/min unless stated otherwise. The counter electrode was a platinum coil. The hydrogen reference electrode (RHE) was manufactured in-house and the hydrogen in the capillary is prepared before each single sample. The compartment of the RHE is contact with the AEM via a luggin capillary. The upper cell compartment of the GDE was filled with as 1 M aqueous KOH (99.995% Suprapur). The measurement protocol with the GDE half cell is described in detail in Table S1.

Cleaning procedure

Before each experiment the upper cell compartment is boiled two times in a glass beaker with 18.2 M Ω deionized water and rinsed with 18.2 M Ω deionized water. To avoid contamination, the cell is stored in 18.2 M Ω deionized water in a sealed glass container between the experiments. When changing to a new catalyst layer composition, the cell is soaked into Nochromix[®] overnight, then extensively rinsed in 18.2 M Ω deionized water before being transferred into a beaker for the boiling procedure.

Electrochemical Protocol

For each data GEIS polarization curve at least two samples are tested. The electrochemical protocol for the GDE ORR testing is adapted from the community standard protocol.² The last data point of each galvanostatic step is iR-compensated by taking a EIS at each galvanostatic step. The value for uncompensated resistance is the magnitude of the impedance, for which the phase angle is closest to 0 in the high frequency region > 1000 Hz. Typically the solution resistance was below 1 Ω .

	Step	Electrochemical		Parameters
		Technique		
1	Preconditionin g (N ₂)	Cyclovoltammograms	Gas purge (Flow rate) Purge duration Potential limits Scan rate Number of cycles	N ₂ (300 mL/min) 15 min 0.06 – 1.1 V vs. RHE 50 mV/s, 500 mV/s 10 each
2	Polarization Curve (O ₂)	Galvanostatic steps coupled with impedance spectroscopy (GEIS)	Gas purge (Flow rate) Purge duration Current steps (hold time)	O ₂ (300 mL/min) 10 min - 0.1 mA/cm ² (90 s), - 1/-2.5/-5/- 10 mA/cm ² (30 s), - 25/-50/-10/-250 mA/cm ² (5 s) - 0.5/-1.0/-1.5/-2.0
			EIS frequency range iR-compensation	A/cm² (5 s) f = 10 kHz – 1 Hz 100% post-correction

Table S1: Electrochemical protocol for the GDE ORR testing ²

Catalyst	lonomer/Membrane	Potential @ 1 A/cm ² (V)	^² Loading (mg/cm²)	Ref
Pajarito Powder	Piperion lonomer / Sustainion Membrane	0.73	1.2	3
FeXK Powder	Sustainion Ionomer / Sustainion Membrane	0.64	1.05	4
Pajarito Powder	Aemion lonomer	0.57	1.6	5
This work Film (70 μm)	Sustainion Ionomer / Sustainion Membrane	0.70	8.59	

Table S2. Performance Comparison of Fe-N-C Catalysts Tested in Gas Diffusion Electrode Configurations

2. Supplementary figures



Figure S1: Pore size distribution of SiO₂ templated carbon films before and after etching.



Figure S2: a) Thermomechanical analysis of mesophase pitch. b) Elemental contamination of the mesophase pitch with elements listed that deviate by 10% from the blank sample in ICP-MS.



Figure S3: Optimization of the PS loading in the film.

	Pristine MP	Oxidative stabilized	Carbonized film (900°C)
	film	film (210°C)	
Conductivity	4.02x10 ⁻⁶	2.14x10⁻⁶	3.02
(S/m)			

Figure S4: Conductivity measurements of the film at stages in preparation sequence.



Figure S5: Effect of the heating rate on the brittleness of the macroporous carbon film at 0.1 C/min (a), 0.5 C/min (b), 1 C/min (c). (Snapshot at maximum bending from video recording)



Figure S6: SEM images of ball milled BM-Film-N₂.



Figure S7: a) Optimization of the FePc loading on Vulcan XC 72 with LSV in RDE in oxygensaturated 0.1 M KOH at 1600 rpm with a scan rate of 10 mV/s for Fe wt% loadings of 0.25 wt%, 0.5 wt%, 1 wt% and 2 wt%. b) Mass Activities at 0.85 V. c) Iron content measured by ICP-MS for the samples with different Fe wt% loading.



Figure S8: a) Determination of the catalyst layer mass loading of the film samples. b) Preparation of the \emptyset = 3 mm sample for the GDE testing with laser cutting.



Thickness: 30 μm (Doctor blade: 500 μm)



Thickness: 50 μm 2 mg/cm² FePc/Vulcan XC 72



Thickness: 70 μm (Doctor blade: 1000 μm)



Thickness: 100 μm 4 mg/cm² FePc/Vulcan XC 72

Figure S9: Determination of the catalyst thicknesses for the $FePc/Film-N_2$ (upper row) and

FePc/Vulcan XC 72 (bottom row) cathode catalyst layers.



Figure S10: First GEIS polarization curve and second repetition of GEIS protocol for the high current density steps. In both it is stepped from lower current densities to higher current densities.



Figure S11: SEM images of Vulcan XC 72 showing the primary particle size of 20 to 50 nm.



Figure S12: SEM images of Film-1% O₂.



Figure S13: XRD pattern of the freestanding catalyst layer, FePc supported on macroporous carbon film- N_2 .



Figure S14: XPS spectra of the freestanding catalyst layer, FePc supported on macroporous carbon film- N_2 .



Figure S15: N_2 sorption isotherms of Film- N_2 and Film-1% O_2 .

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