Electronic Supplementary Information (ESI)

Meta-kinks are key to binder performance of poly(arylene piperidinium) ionomers for alkaline membrane water electrolysis using non-noble metal catalysts [†]

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Materials

m-terphenyl (BLD Pharm, 99.5%), *p*-terphenyl (Acros Organics, 99%), *N*-methyl-4-piperidone (MePip, BLD Pharm, 98.27%), 2,2,2-trifluoroacetophenone (ABCR GmbH, 98%), dichloromethane (DCM, Fisher Scientific, 99%), trifluoroacetic acid (TFA, ABCR GmbH, 99.9%), trifluoromethanesulfonic acid (TFSA, ABCR GmbH, 99%), dimethyl sulfoxide (DMSO, Fisher Scientific, 99.9%), DMSO- d_6 (Deuteron GmbH, 99.8%), potassium chloride (Fisher Scientific, 99%), potassium hydroxide (Fisher Scientific, 85%), *N*-methyl-2-pyrrolidone (NMP, ABCR GmbH, 99%) methyl iodide (MeI, Thermo Scientific, 99%), *N*,*N*-diisopropylethylamine (DIPEA, Carl Roth GmbH, 99%) ethyl acetate, *N*,*N*-dimethylformamide (Fisher Scientific, 99.5%) and ammonium trifluoroacetate (Thermo Scientific, 98%) were all used as received. Nafion was obtained from Sigma-Aldrich.

Synthesis

Synthesis of poly(terphenylene piperidinium) and subsequent quaternization

Polymers of the Mx series were synthesized according to literature.^{1,2} The synthesis of M0 is presented as an example. N-methyl-4-piperidone (1.92 g, 17.0 mmol), 2.2.2trifluoroacetophenone (0.52 g, 3.0 mmol) and p-terphenyl (4.00 g, 17.4 mmol) were added to a 100 ml 2-neck round bottom flask equipped with a mechanical stirrer. Subsequently, DCM (18.1 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (1.3 mL, 1.7 mmol) and TFSA (15.3 mL, 174 mmol) were added. The mixture was stirred at 0 °C during 40 h. The mixture was poured into an excess of deionized water at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Subsequently, this precursor-polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (100 mL) and NMP (100 mL), DIPEA (14.8 mL, 85 mmol, 5 eq. regarding MePip) and MeI (5.3 mL, 85 mmol, 5 eq. regarding MePip) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solid was filtered off and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual N,N-diisopropylethyl ammonium salts. After drying under ambient conditions, the guaternized polymer was collected in guantitative yield.

Synthesis of NiFe as layered double hydroxide (LDH) with molar nickel

Iron ratio of 5 : 1 was prepared with a microwave assisted one-pot synthesis is conducted using 1200 μ L of 0.6 M Ni(OAc)₂*4H₂O and 240 μ L of 0.6 M Fe(NO₃)₃*9 H₂O precursor solution, added to 6 mL DMF and stirred subsequently. 4 mL DMF and 8 mL ultrapure water were added. The resulting solution was transferred to a microwave and reacted with constant stirring for 60 min at 120 °C and 160 °C for 30 min. The product was collected, washed with ethanol and Mili-Q and finally dried in a freeze dryer. NiFe-LDH resulted in a Ni/Fe ratio of 3.25 ± 0.07.

Molecular characterization

NMR spectroscopy. ¹H-NMR spectra were recorded on polymer in DMSO- d_6 (δ ¹H = 2.50 ppm) solutions containing a few drops of trifluoroacetic acid, to protonate any tertiary amines as well as causing a downfield shift of the water signal, using an Avance NEO 600 FT Spectrometer (600 MHz).

Size Exclusion Chromatography (SEC). Molecular weights were measured on a Shimadzu system comprising a 10 μ m PSS GRAM guard column and three PSS GRAM columns with pore sizes ranging from 30 to 10³ Å, connected in series with a RID20A refractive index detector and an SPD-40V UV-vis detector (Shimadzu). Calibration was done with polystyrene standards. A 0.1M solution of ammonium trifluoroacetate in DMF was used as eluent at 70 °C with a flow rate of 1.0 mL·min⁻¹.

Brunauer-Emmett-Teller (BET) gas sorption measurements

The nitrogen adsorption–desorption isotherms were recorded at 77 K using an Autosorb IQ2 sorptimeter from 3P Instruments. Specific surface areas were calculated by BET gas sorption measurements, and the pore size distributions were calculated from the adsorption isotherm using the quenched solid density functional theory method assuming slit-type pores.

Membrane preparation and characterization

Membranes of ~ 100 μ m thickness were prepared by doctor-blading DMSO solutions (30 *wt*-%) onto flat glass substrates. After drying the wet films at 60 °C for 20 hours under ambient pressure, they were removed from the substrate by immersion into water. After treatment with 1 M potassium chloride solution and extensive washing with deionized (DI) water at elevated temperature (60 °C) the chloride form of the polymer was obtained, which was kept immersed in DI water until further characterization.

Thermal gravimetric analysis (TGA). TGA was measured on membrane samples in chloride form under nitrogen atmosphere using a Thermogravimetric Analyzer from Perkin Elmer Company. Samples were heated to 120 °C and kept isothermally at this temperature during 30 min, after which they were cooled to 30 °C. Lastly, the samples were heated to 650 °C with a heating rate of 10 °C min⁻¹.

Tensile testing. Stress-strain experiments of membranes in chloride form were carried out at ambient conditions using a Linkam TST-350 with a displacement ramp of 5 μ m s⁻¹. These measurements were carried out on dog bones of membranes prepared using a cutting die in which the gauge was 15 mm × 2 mm. The ultimate tensile strength (UTS) and elongation at break (ϵ_b) were taken as the stress and strain, respectively, at the point of sample breaking. The Young's modulus was obtained by linear regression of the initial linear part in the stress-strain curves.

Water uptake (WU) and swelling ratio (SR). The water uptake and swelling ratio of the membranes, in chloride form, were measured under immersed conditions. Membrane pieces, of each sample were immersed in deionized water. After 1 d of storage at room temperature, the membranes were removed from the water, gently wiped with tissue paper and weight, length, width and thickness were determined. This was then repeated after 1 d of storage at 40, 60, and 80 °C, respectively. Subsequently, the membranes dried under vacuum at 60 °C during 2 d. The dry membranes were weighed and the water uptake was calculated as the mass increase of the wet membranes divided by the dry weight. From these values, the hydration number, defined as the molar concentration of water divided by thy concentration of hydroxide ions, was calculated by dividing the water uptake with the product of the theoretical ion-exchange capacity (IEC, in chloride form) times the molar mass of water.

The water uptake of the membrane, in hydroxide form, was measured under immersed conditions. Membrane pieces, of each sample, in chloride form were ion-exchanged to hydroxide form by immersion in carbon dioxide free 1 M sodium hydroxide solution during 3 d at room temperature. Then, the membranes were first extensively washed with and then stored in degassed deionized water. After 1 d of storage at room temperature, the membranes were removed from the water, gently wiped with tissue paper, and weighed. This was then repeated after 1 d of storage at 40, 60, and 80 °C, respectively. Subsequently, the membranes were ion-exchanged to chloride form by immersion in an aqueous 1 M KCl solution during 3 d at 60 °C, after which they were extensively washed with deionized water and dried under vacuum at 60 °C during 2 d. The dry membranes, in chloride form, were weighed, and their weight in hydroxide form was calculated by multiplying the noted weights with the ratio of the molar mass of the repeating unit in hydroxide form divided by the molar mass in chloride form. The water uptake was calculated as the mass increase of the wet membranes divided by the dry weight. From these values, the hydration number, defined as the molar concentration of water divided by thy concentration of hydroxide ions, was calculated by dividing the water uptake with the product of the theoretical ion-exchange capacity (IEC, in hydroxide form) times the molar mass of water.

Additionally, the width, length and thickness of the dry membranes, in chloride form, were determined and the in-plane swelling ratio was calculated by the areal increase divided by the dry membrane area; the through-plane swelling ratio was calculated by the thickness increase divided by the dry membrane thickness.

Ion conductivity (\sigma). Membrane samples, in chloride form, were clamped into a four-electrode in-plane conductivity cell (BekkTech BT-110, Scribner) immersed in water. The membrane resistance (*R*) was measured at 30, 50, 70 and 90 °C by linear sweep voltammetry over the range of 100 mV to -100 mV with a scan rate of 50 mV s⁻¹. Membrane samples, in hydroxide form, were clamped into a four-electrode in-plane conductivity cell immersed in water which was constantly de-aerated with argon, as previously reported.^{3–5} To remove all carbonates from the membranes, a current of 0.1 mA was applied over the inner electrodes. Every 30 min, electrochemical purging was stopped, and several linear voltage sweeps were conducted over the range of 100 mV to -100 mV with a scan rate of 50 mV s⁻¹ until the resistance reached a constant value. The membrane resistance (*R*) was measured at 25, 40, 60 and 80 °C by linear sweep voltammetry over the range of 100 mV to -100 mV s⁻¹.

Chloride conductivities in humid atmosphere (95% r. h.) were recorded in in-plane mode using a temperature and humidity-controlled chamber equipped with a four-point probe (MK3 FUMATECH GmbH, Germany) at 30, 50, 70 and 90 °C and ambient pressure. The samples were equilibrated at the respective temperature for 2 h before starting the measurements. The distance between electrodes L was 1 cm and the sample width W 2 cm. The membrane resistances R were obtained from galvanostatic impedance spectroscopic measurements with a Gamry Reference 600 potentiostat (Gamry Instruments; US) in the frequency range from 1 MHz to 1 Hz. The R values were taken at the frequency that produced minimum imaginary response (phase angle close to zero).

Ion conductivity was determined by the following equation:

 $\sigma = L \cdot (R \cdot W \cdot T)^{-1}$

where L is distance between the voltage-sensing electrodes (set at 0.425 cm), W is the width of membrane, and T is membrane thickness after immersing in deionized water at room temperature.

RDE scale electrochemical testing: experimental details and setup

The electrochemical investigations of the binder materials were conducted using the below electrochemical parameters. An image of the used RDE setup is given in Figure S1.

Step	Technique	Parameters
1.	CA	1.1 V vs RHE, 10 minuets
2.	PEIS	1.1 V vs RHE; 1 MHz – 1.000 mHz
3.	CV	1.1 V vs RHE – 1.7 V vs RHE; 5 mV s ⁻¹ ; two cycles
4.	CV	1.1 V vs RHE – 1.7 V vs RHE; 50 mV s ⁻¹ ; 20 cycles
5.	CV	1.1 V vs RHE – 1.7 V vs RHE; 5 mV s ⁻¹ ; two cycles
6.	PEIS	1.1 V vs RHE; 1 MHz – 1.000 mHz
7.	CA	1.1 V vs RHE; 10 minutes

Table S1 Protocol for the investigation of the electrochemical activity towards OER in RDE.

CA: chronoamperometry, PEIS: potentiostatic electrochemical impedance spectroscopy, CV: cyclic voltammetry.

Step	Technique	Parameters
1.	СА	1.1 V vs RHE, 10 minuets
2.	PEIS	1.1 V vs RHE; 1 MHz – 1.000 mHz
3.	CVA	1.23 (1.43) V vs RHE – 1.7 V vs RHE; 100 mV s ⁻¹ ; 10 s at initial and final
		potential; 2000 cycles
4.	CV	1.1 V vs RHE – 1.7 V vs RHE; 50 mV s-1; two cycles
5.	PEIS	1.1 V vs RHE; 1 MHz – 1.000 mHz
6.	СА	1.1 V vs RHE; 10 minutes
7.	СА	1.1 V vs RHE; 10 minutes

Table S2 Protocol for the investigation of electrochemical stability of the applied materials in RDE.

CA: chronoamperometry, PEIS: potentiostatic electrochemical impedance spectroscopy, CVA: cyclic voltammetry advanced, CV: cyclic voltammetry.



Fig. S1 Image of the applied RDE setup. a: working electrode (WE); b: reference electrode (Ref; RHE); c: counter electrode (CE); A: main compartment; B Luggin cappilary.

Scanning electron microscopy

Scanning electron microscope (SEM) measurements were done with a Zeiss Gemini 982 instrument at ZELMI Centrum, Technical University of Berlin.

Additional Figures



Fig. S2 ¹H NMR spectra of Mx polymers in DMSO- d_6 with 10 vol-% TFA.



Fig. S3 Comparison of Mx 1 H NMR spectra's aromatic regions.



Fig. S4 SEC elution curves of Mx polymers in DMF/NH₄TFA, calibrated against polystyrene.



Fig. S5 Swelling ratio at 90 °C (a) and hydration numbers of chloride forms (b).



Fig. S6 BET isotherms of M100 (a), M50 (b) and M0 (c).



Fig. S7 Chloride conductivities depending on the number of *meta*-kinks in the polymer backbone: a) measured at variable temperatures, b) Arrhenius plots; c) chloride conductivities depending on the hydration number and the corresponding slopes depending on the percentage *m*-terphenyl in the polymers (d).



Fig. S8 Chloride conductivities under RH of 95 %.



Fig. S9 TGA traces of the PAP polymers.



Fig. S10 Stress-strain curves of the polyelectrolytes in chloride form under ambient conditions.



Fig. S11 a) OER activities for differently kinked binder polymers in RDE with NiFe-LDH catalyst. Cycle stability of RDEs prepared with M100 (b), M50 (c) and M0 (d) as binder polymers.



Fig. S12 Nyquits plots to evaluate the impedance of NiFe-LDH with M100 as binder in 0.1 M KOH and 1 M KOH. The measurements were conducted in N_2 purged KOH solution at RT and a rotation speed of 1600 rpm.

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