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Supplementary Information

Exceptional durability enhancement of PA/PBI based polymer electrolyte membrane fuel cells for high temperature operation at 200 °C

David Aili,[a] Jin Zhang,[b] Mark Tonny Dalsgaard Jakobsen,[a] Haijin Zhu[c], Tianyu Yang,[d] Jian Liu,[b] Maria Forsyth,[c] Chao Pan,[a] Jens Oluf Jensen,[a] Lars Nilausen Cleemann,[a] San Ping Jiang[b,*] and Qingfeng Li[a,*]

[a] *Section for Proton Conductors, Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Lyngby, Denmark*

[b] *Fuels and Energy Technology Institute & Department of Chemical Engineering, Curtin University, Perth, Western Australia 6102, Australia*

[c] *Institute for Frontier Materials, Deakin University, Geelong, VIC 3220, Australia*

[d] *Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, Brisbane, QLD 4072, Australia*

Email: Prof. Qingfeng Li (qfli@dtu.dk), Prof. San Ping Jiang (s.jiang@curtin.edu.au)

S1 Experimental

S1.1 Membrane preparation

The PWA-*meso*-SiO_2 (40 wt% PWA, 2.0 g) was prepared as described elsewhere.[1] It was dispersed in 100 mL methanol containing 2.0 g dequalinium chloride hydrate (DCH, Sigma-Aldrich, see Scheme S1) and the mixture was stirred mechanically for 1 hour followed by ultrasonication for 3 hours to form a fine dispersion. The mixture was subsequently dried at 160 °C for 20 hours *in vacuo* yielding an off-white powder. Composite membranes were prepared by dispersing the modified PWA-*meso*-SiO_2 in a *N*,*N*-dimethylacetamide (DMAc) solution of poly[2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole] (PBI, see Scheme S1) (6.1 wt%) from Danish Power Systems (inherent viscosity 0.95 dL g^{-1} at 30.0 °C and 500 mg dL^{-1} in 96 wt.% H_2SO_4), to give PWA-*meso*-SiO_2:PBI weight ratios of 0, 5, 10, 15, 20, 30 and 40 wt%. The mixtures were ultrasonicated for 20 hours and cast on Petri dishes followed by heating from room temperature to 120 °C with a heating rate of 7 °C h^{-1}. The obtained composite membranes were treated with methanol at 50 °C in order to wash out the DCH modifier and further dried at 180 °C for 3 hours. The membranes were imbibed with phosphoric acid in 85 wt% H_3PO_4 (Sigma-Aldrich) at room temperature for at least 2 weeks.

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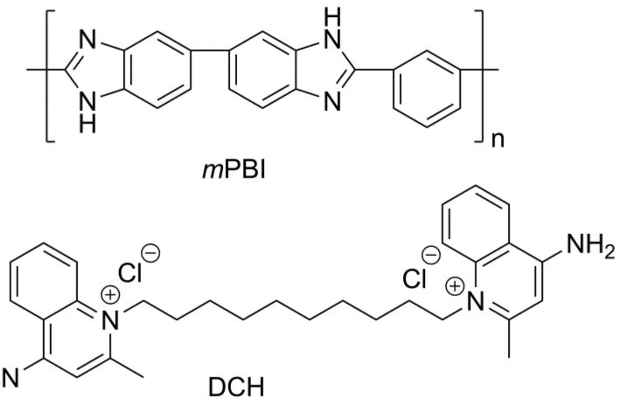
[1] H. Tang, M. Pan, S. Lu, J. Lu and S. P. Jiang, *Chem. Commun.*, 2010, **46**, 4351-4353.



Scheme S1 Chemical structure of the poly[2,2′-m-(phenylene)-5,5′-bisbenzimidazole] (PBI) repeat unit and of the dequalinium chloride hydrate (DCH) modifier.

S1.2 Characterization

S1.2.1 Physicochemical properties and imaging

Microstructure and element distribution of PWA-*meso*-SiO_2 powders were examined by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) using FEI Titan G2 STEM with an applied acceleration voltage of 200 kV. The powder was dispersed in hexane and dropwise added onto a copper grid for the HAADF STEM characterization. The N_2 adsorption/desorption isotherms of *meso*-SiO_2 and PWA-*meso*-SiO_2 were measured with a Tristar II BET instrument after degas treatment at 80 °C overnight. All the single pulse ^1H NMR and the ^1H PFG-NMR diffusion experiments were carried out on a Bruker Advance III 300 MHz wide bore spectrometer (with proton Larmor frequency of 300.13 MHz) equipped with a 5 mm diff50 pulse-field gradient (PFG) probe. The 90° pulse lengths for single pulse ^1H NMR were 15 μs, and the recycle delays were 10s to allow the system to recover to the equilibrium state. The pulse-field gradient stimulated echo (PFG-STE) pulse sequence was used to obtain diffusion coefficients. The maximum gradient strength is 29.454 T m^{-1}. The sample temperatures in the probe for the ^1H NMR variable temperature experiments were calibrated by using the relative chemical shift separation between the OH resonance and CH_3 resonance of dry methanol. The acid uptake and volume swelling were determined gravimetrically and volumetrically, respectively. Scanning electron microscopy (SEM) imaging was carried out using a Carl Zeiss EVO MA10 scanning electron microscope equipped with an INCA energy-dispersive X-ray spectroscopy (EDS) system from Oxford Instruments. Membrane cross-sections for SEM imaging were prepared by sandwiching the membrane samples between two pieces of non-woven carbon cloth followed by ion-milling using a Hitachi E-3500. Subsequently, the membrane samples were sputter coated with carbon. Thermogravimetric data were acquired using a Netzsch STA 409 PC. The thermograms were recorded at a heating rate of 10 °C min^{-1} in air. The thermogravimetric curves were normalized relative to the dry membrane at 210 °C. Stress–strain curves were recorded using a Testometric Micro 350 under ambient conditions with a crosshead speed of 10.00 mm min^{-1}. The specimens were die-cut to a dog-bone shape with a gauge length and width of 28 and 2 mm, respectively.

S1.2.2 Membrane-electrode assembly preparation and fuel cell tests

The gas diffusion electrodes were supplied by Danish Power Systems. They consisted of 57.33 wt.% Pt/C from Johnson Matthey, applied on a nonwoven carbon substrate (Freudenberg H2315 C2) by a spray technique using PBI as binder. The platinum loading on both anode and cathode was 1.6 mg cm^{-2} using 0.1 mg cm^{-2} *m*PBI as the binder. Membrane-electrode assemblies (MEAs) with an active area of 4 cm^2 were fabricated by sandwiching the phosphoric acid doped membrane between two pieces of the gas diffusion electrodes followed by hot-pressing (4.9 MPa) at 180 °C for 10 minutes.

Each MEA was tested as a single cell with fuel cell hardware of graphite flow plates with parallel gas channel (2 mm wide, 1 mm deep, and 1 mm wide ribs). The flow plates were positioned with a perpendicular flow field such that the flow direction of the gases was in a cross flow orientation. 150 µm of PTFE was used for gas sealing between the MEA and the flow plates on both sides of the MEA. 1 mm of Papyrex was used for gas sealing between the flow plates and the applied silver- or gold coated current collectors. On the other side of the current collectors, 1 mm thick layers of Viton seals were used for electrical insulation. Two square aluminum end plates were used to clamp the MEA, flow plates, current collecting plates, and seals together. Four bolts, one in each corner of the end plates, were tightened to a torque of 1 Nm.

The fuel cells were mounted onto individual channels of an in-house build test rack, which is capable of simultaneously testing up to 12 single cells in parallel with a maximum load capacity of 20 A per cell. Both end plates of each cell was equipped with heaters and the setpoint temperature was maintained using a EUROTHERM PID temperature controller which received input signal from a type K thermocouple inserted into one of the endplates. Hydrogen and air (decompressed from 5-7 bar) were supplied to the fuel cell at ambient pressure without pre-humidification. The flow rates were controlled using 1355 Sho-Rate variable area flow meters equipped with SS 316 floaters and measurement tubes of model F5 and A5 for Air and hydrogen, respectively. The flow meters had been calibrated against a Bios Definer 220 with an accuracy of ±1 %. The electrochemical characteristics of each cell was controlled and monitored with Labview.

During life time analysis, the cells were operated galvanostatically at 200 mA cm^{-2} with the temperature controlled at 200 °C. The applied flow rate of hydrogen and air was 45 (±9 %) nmL min^{-1} and 176 (±8 %) nmL min^{-1}, respectively, corresponding to a stoichiometry λ of 7.3-8.8 and

12.2-14.3 at 200 mA cm^{-2} for hydrogen and air, respectively. Periodic polarization curves were measured from 0 mA cm^{-2} (10 min) to 1000 mA cm^{-2} by means of current step potentiometry with a stabilization time of 2 min at each current step. The scan sequence was terminated if the cell potential reached 0 V. During measurement of polarization curves, the flow rates were changed accordingly to account for the higher current. The polarization data used for the calculation of the *in-situ* conductivity (Fig. 2A) of the composites in the whole composition range were acquired using parallel test setup equipped with a Thorpe tube flowmeter for the feed gases.

The area specific resistance was obtained from the polarization data in the linear region where no mass transport limitations were present by means of fitting to Equation S1 using non-linear regression. In Equation S1, E is the cell voltage, i is the current density, a is a constant, b is the Tafel slope and R_{ASR} is the area specific resistance.

$$E = a - b\log(i) - iR_{ASR} \qquad \text{(Eq. S1)}$$

The *in-situ* cross-sectional proton conductivity of the composite membranes, σ, was subsequently calculated according to Equation S2, where t is the thickness of the membrane as measured subsequent to acid doping and R_{ASR} is the area specific resistance as obtained from Equation S1. For the data presented in Figure 3C, linear regression on the linear region of the polarization curves was used to obtain R_{ASR}.

$$\sigma = t / R_{ASR} \qquad \text{(Eq. S2)}$$

S2 Results

Table S1 Phosphoric acid uptake and volume swelling after doping in 85 wt% H_3PO_4 at room temperature for at least 2 weeks.

PWA-*meso*-SiO_2 loading / wt%	0	5	10	15	20	30	40
H_3PO_4 uptake / wt%	341	308	284	242	226	219	215
Volume swelling / vol%	203	167	163	137	128	130	100

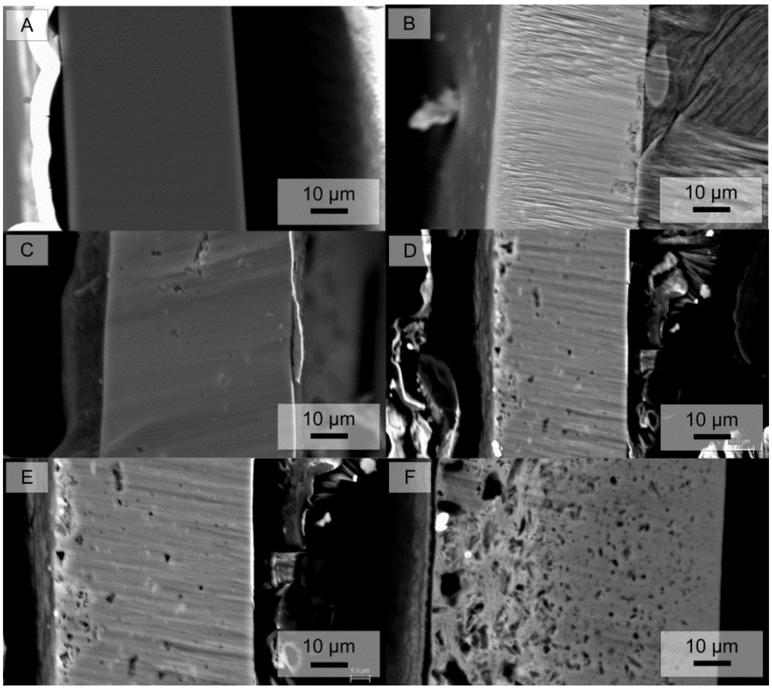


Fig.S1 Cross-sectional scanning electron micrographs (secondary images) of the PBI membranes with PWA-*meso*-SiO_2 loadings of 0 wt.% (A), 5 wt.% (B), 10 wt.% (C), 15 wt.% (D), 20 wt.% (E) and 40 wt.% (F).

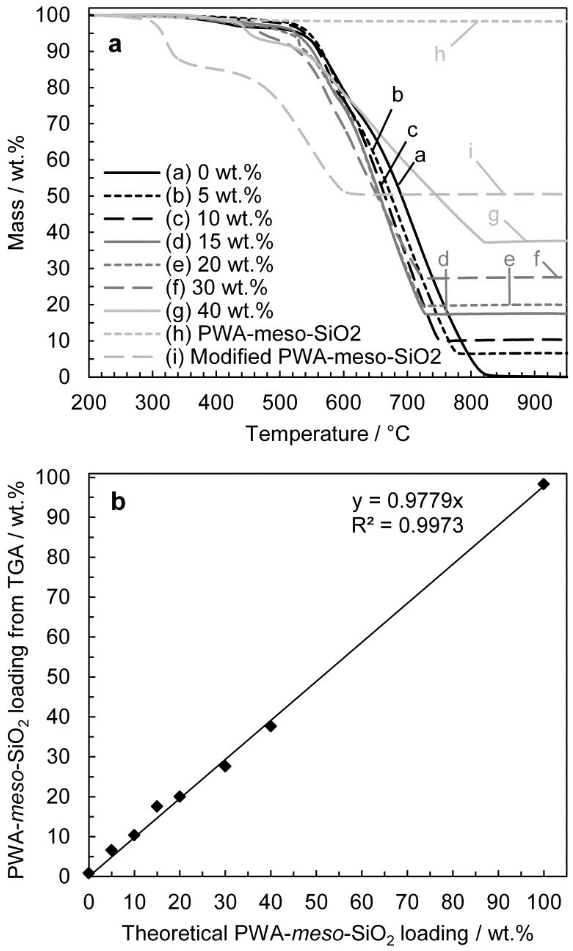


Fig.S2 (a) Thermogravimetric curves of the composite membranes with PWA-*meso*-SiO_2 loadings ranging from 0-40 wt.% (curve a-g) and of the pristine and DCH modified PWA-*meso*-SiO_2 (curve h and i, respectively). (b) Theoretical PWA-*meso*-SiO_2 loading corresponding to the amount PWA-*meso*-SiO_2 added to the membrane casting solution versus the PWA-*meso*-SiO_2 content of the resulting composite membrane as determined with TGA.

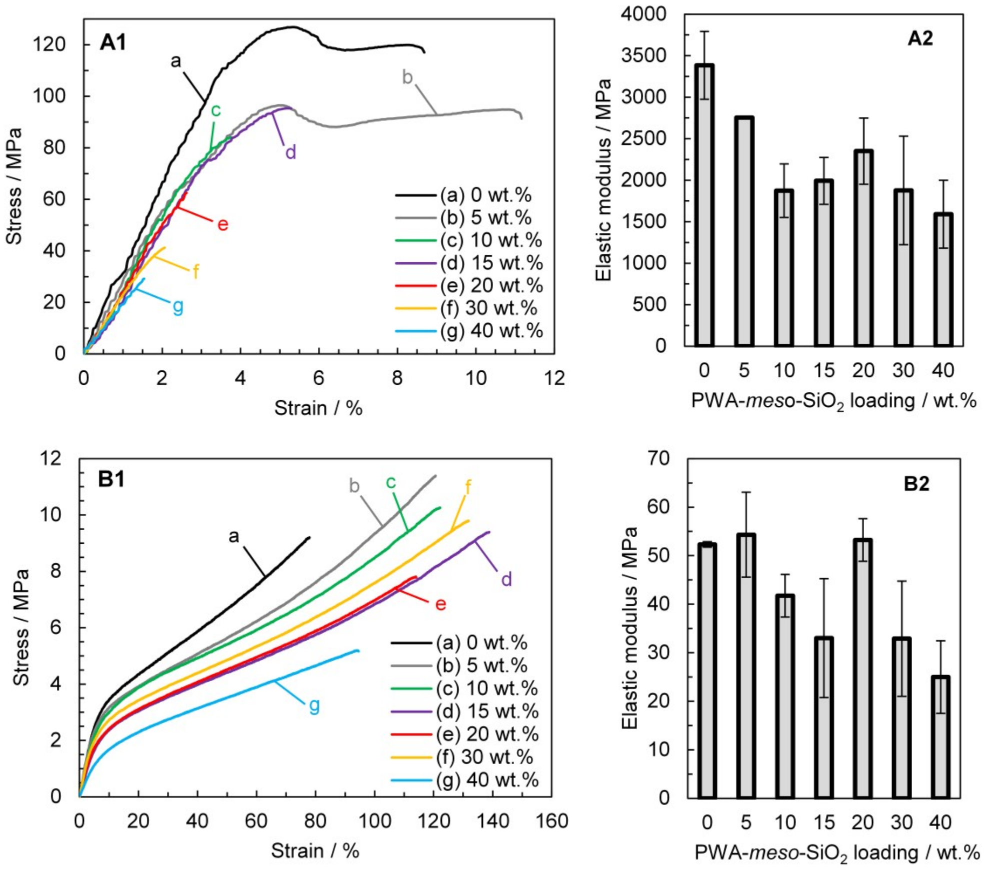


Fig. S3 Selection of stress-strain curves for the composite membranes with PWA-*meso*-SiO_2 loadings of 0-40 wt.% before (A1) and after (B1) phosphoric acid doping. The corresponding elastic modulus for each membrane type before (A2) and after phosphoric acid doping (B2), where the heights of the gray bars represent the average values. The standard deviations are indicated by the error bars.

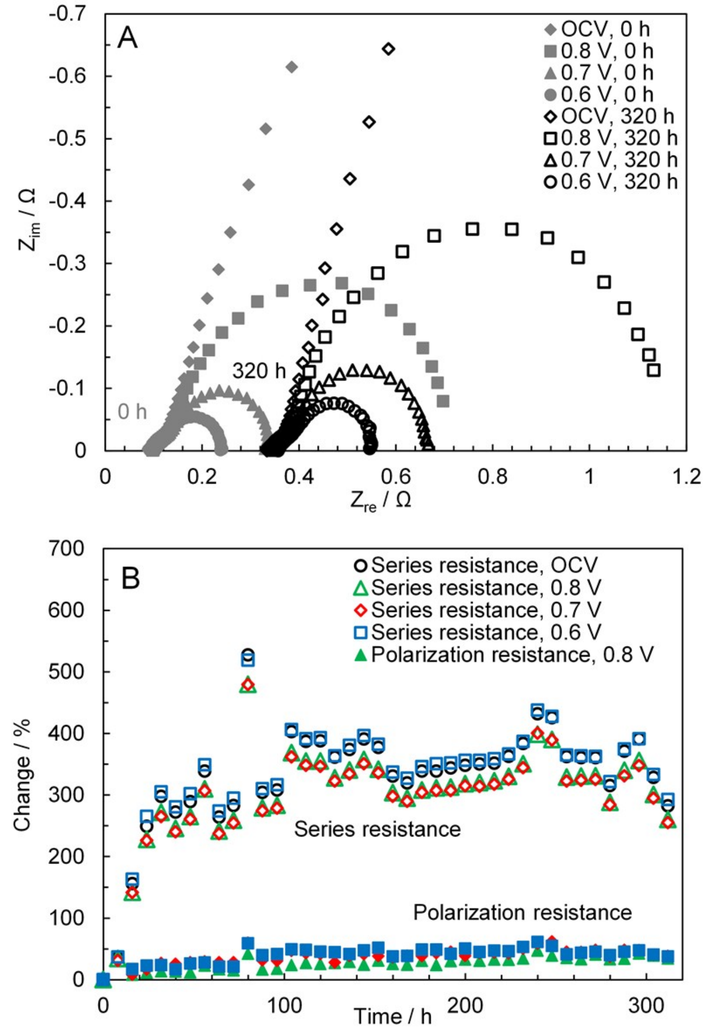


Fig. S4 (A) Electrochemical impedance spectra at open circuit voltage (OCV), 0.8, 0.7, and 0.6 V of a 4 cm^2 pristine PA/PBI cell operating with hydrogen and air at 200 °C after 0 and 320 h at constant current (200 mA cm^{-2}); (B) Variation of the series resistance and polarization resistance as a function of time.

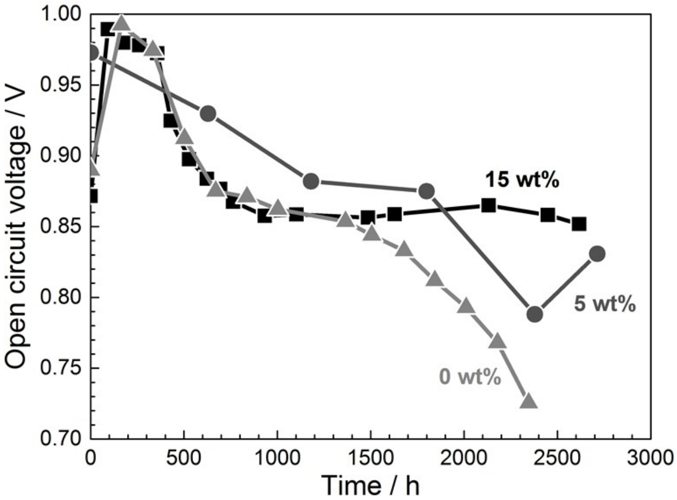


Fig. S5 Variation of the open circuit voltages for fuel cells based on PA/PBI membranes containing 0, 5, and 15 wt.% PWA-*meso*-SiO_2. The cells were operated with hydrogen and air at 200 mA cm^{-2} and 200 °C.