

Supporting information

NMR analysis of phosphoric acid distribution in porous fuel cell catalysts

En Zhang^{a†}, Natalia Fulik^{b†}, Hanyue Zhang^a, Nico Bevilacqua^c, Roswitha Zeis^c, Fei Xu^a, Eike Brunner^b and Stefan Kaskel^{a*}

^a Chair for Inorganic Chemistry I, TU Dresden, 01069, Dresden, Germany.

^b Chair for Bioanalytical Chemistry, TU Dresden, 01069, Dresden, Germany.

^c Karlsruhe Institute of Technology (KIT), Helmholtz Institute Ulm (HIU), Helmholtzstraße 11, 89081, Ulm, Germany.

*Corresponding author: stefan.kaskel@tu-dresden.de

Materials. Novoloid based active carbon fiber (C_{micro}) was provided by Kynol Europe GmbH. YP50F (C_{broad}) is coconut-based activated carbon from Kuraray. Phosphoric acid was bought from Grüssing GmbH. The Pt@Vulcan sample was obtained by scratching off a spray-coated commercial Vulcan XC-72-based electrocatalyst layer (20wt% Pt, QuinTech) from the gas diffusion layer. Mesoporous carbon C_{meso} was prepared by a hard-templating method. Firstly, 2.0 g of SBA-15 was infiltrated with a mixture of 2.1 ml of SMP-10 and 0.5 ml of p-divinylbenzene. Thereafter, the sample was carbonized under Ar in a horizontal tubular quartz furnace at 800 °C with a heating rate of 60 °C h⁻¹ for 2 h. The silica template was washed out with hydrofluoric acid for 24 h and the obtained materials were washed with water and ethanol several times. Thereafter the obtained material was chlorinated at 900 °C in a tubular quartz furnace with a heating rate of 450 °C h⁻¹ under a mixed Ar-Cl₂ gas mixture (80 ml Ar min⁻¹ and 70 ml Cl₂ min⁻¹) for 3 hours. Subsequently the furnace was cooled down to 600 °C with subsequent H₂ reduction for another 1 h to remove the adsorbed Cl₂.

Characterization. Nitrogen physisorption was conducted at 77 K on a Quadrasorb and a BELSORP instrument. The Brunauer-Emmett-Teller (BET) method was used to quantify the specific surface area based on adsorption data in a relative pressure range 0.05 < P/P₀ < 0.20 and the total pore volume and the pore size distribution were calculated applying quenched solid density functional theory (QSDFT). For microporous carbon, slit pores were modelled and for mesoporous carbon slit/cylindrical pores were modelled using the equilibrium branches of the isotherms. The samples were activated at 150 °C overnight prior to the measurement.

NMR measurements. Carbon materials were loaded with 85% phosphoric acid by the incipient wetness method. The volume of added acid was calculated to exactly fit varying degrees of pore filling for investigating the exchange between free and adsorbed states. Solid state ¹H and ³¹P NMR spectra were acquired on a Bruker AVANCE 300 spectrometer using 2.5 mm double resonance (¹H, X) MAS NMR probe head. The ¹H was referenced relative to tetramethylsilane (TMS). For experiments, 90° single pulse excitation and HPDEC pulse program was applied with 3.1 μs pulse length and 3 s. For each sample, 8 scans were acquired. The ³¹P spectra were referenced relative to phosphoric acid and TMS, respectively. The experiments were performed with 90° single pulse excitation with 3.5 μs pulse length and 40 s recycling delay. For all samples, 128 spectra were recorded. The spinning rate was 16 kHz for all samples. During measurements, SPINAL64 ¹H decoupling was used.

Table S1. The porosity of the measured carbon materials.

Carbon	Specific pore volume cm ³ g ⁻¹	Surface area m ² g ⁻¹	Peak pore size nm
C_{broad}	0.74	1624	0.91/3.3
C_{micro}	0.36	806	0.87
C_{meso}	1.82	3029	0.95/4.8
Vulcan	0.37	220	broad
Pt@Vulcan	0.32	184	broad

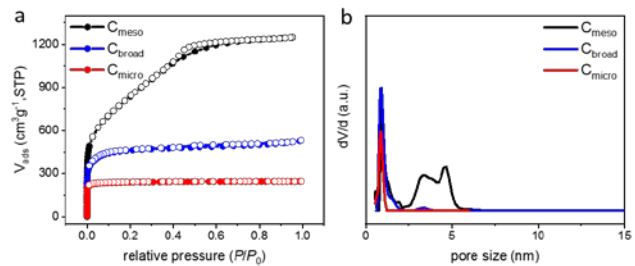


Figure S1. N₂ physisorption of model carbons at 77 K and the corresponding pore size distribution.

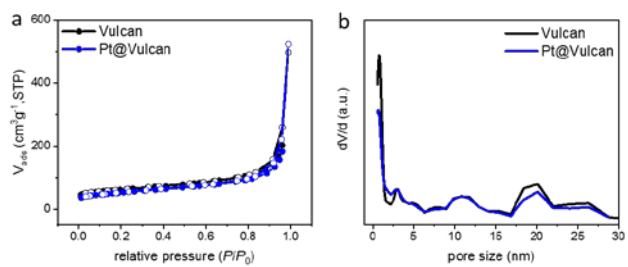


Figure S2. N₂ physisorption of model carbons at 77 K and the corresponding pore size distribution.

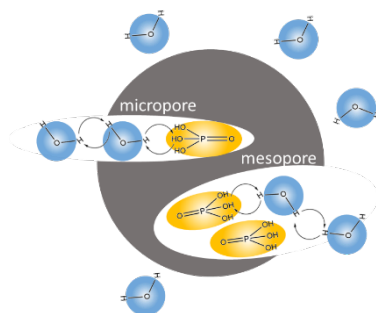


Figure S3. The schematic illustration of phosphoric acid adsorption inside porous carbons.

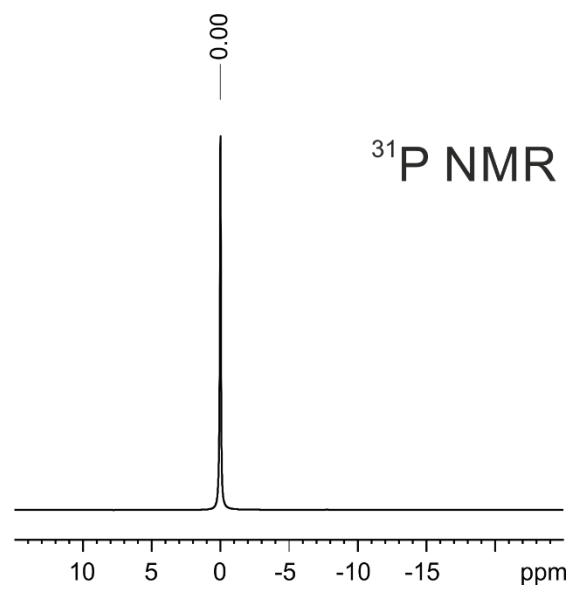
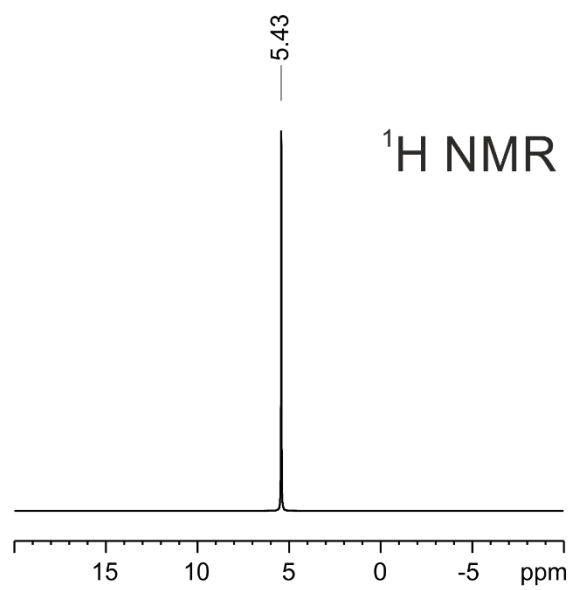


Figure S4. Liquid-state ^1H and ^{31}P NMR spectra of pure bulk 85% phosphoric acid.