Supporting information

Infiltrated mesoporous oxide monoliths as high lithium transference number electrolyte

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Synthesis of monoSiO₂

Porous SiO₂ monolith was prepared according to the sol–gel process reported previously.[1] In a typical preparation, 0.51 g of poly(ethylene glycol) (PEG, M_w =10 000) was dissolved in 5.0 mL of 10 mM acetic acid (HOAc)_{aq}. After obtaining a homogeneous solution, the solution was cooled at 0 °C in an ice-water bath, followed by adding 0.45 g of urea and 2.5 mL of tetramethyl orthosilicate (TMOS) with vigorous stirring. After mixing for 30 min for hydrolysis of TMOS, the solution was kept at 30 °C for 24 h for gelation. The obtained gel was subsequently aged at 80 °C for 48 h.

Then, the gel was washed with ethanol (EtOH)/H₂O (1/1 in volume) at 60 °C for 4 h for 3 times, and dried at 60 °C. The dried gel was subsequently calcined at 600 °C for 2 h at the heating rate of 100 °C h⁻¹.

Post-grafting of monoSiO₂

Prior to post-grafting, the SiO₂ monoliths were dried at 150 °C under vacuum to remove adsorbed H_2O . The dried SiO₂ monoliths were immersed in a series of reaction solutions containing various silane coupling reagents. For the monoSiO₂ grafted with –Si-(CH₃)₃, –(CH₂)₃SO₃H, –(CH₂)₃NH₂ and –(CH₂)₃-N⁺(CH₃)₃Cl⁻, chlorotrimethylsilane (33 wt% in toluene), 3-(trihydroxysilyl)-1- propanesulfonic acid (30 to 35 wt% in H₂O), 3-aminopropyltriethoxysilane (33 wt% in EtOH) and N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (33 wt% in methanol) were employed, respectively. After the reaction at 60 °C for 24 h, the functionalized SiO₂ monoliths were washed with EtOH at 60 °C for 4 h for 5 times followed by drying at 60 °C.

Synthesis of monoAl₂O₃

Porous Al₂O₃ monolith was prepared according to the method reported previously.[2] First, 4.32 g of AlCl₃·6H₂O and 0.070 g of poly(ethylene oxide) (PEO, M_w =1 000 000) was dissolved in the mixture of 4.0 mL of H₂O and 5.5 mL of EtOH. After obtaining a homogeneous solution, 3.75 mL of propylene oxide (PO) was added with vigorous stirring followed by mixing for 30 s at room temperature. Then, the solution was kept at 40 °C for 24 h for gelation and dried at 40 °C. The dried gel was calcined at 600 °C for 2 h at the heating rate of 100 °C h⁻¹.

Characterization of monoSiO₂ and monoAl₂O₃

The microstructures of the fractured surfaces of the samples were observed using scanning electron microscopy and transmission electron microscopy (SEM, JSM-6060S, JEOL; TEM, Philips CM200).

A N₂ adsorption-desorption apparatus (BELSORP-mini II, Bel Japan Inc.) was employed to characterize the pore properties. Samples were degassed at 120 $^{\circ}$ C under vacuum for more than 10 h prior to the measurement.

Thermogravimetric analysis (TGA) was performed by Thermo plus TG 8120 (Rigaku Corp., Japan) at a heating rate of 5 °C min⁻¹ while continuously supplying air at a rate of 100 mL min⁻¹.

Solid state NMR measurements were performed on a Bruker Avance III 400 MHz instrument in a magnetic field of 9.4 T and the Larmor frequencies of 400.1, 100.6 and 79.5 MHz for ¹H, ¹³C and ²⁹Si, respectively. The experiments were performed using a Bruker double resonance 4 mm MAS probe with samples packed in ZrO₂ rotors. All spectra were obtained at the room temperature of about 298 K and the spinning speed of 12500 Hz sufficient to remove the spinning sidebands away from the spectral regions of interest. The ¹H-¹³C and ¹H-²⁹Si Cross-Polarization (CP) MAS spectra were recorded using a ramped spin-locking on proton channel. The contact times were set to 2 and 4 ms for ¹³C and ²⁹Si, found to be close to the optimal. Between 2000 and 8000 accumulations was commonly made in the CP experiments to obtain sufficiently high level of signals. The quantitative measurements for ²⁹Si were carried out by acquiring direct excitation spectra under the MAS conditions with long relaxation delay of 300 s, found to be sufficient for a complete magnetization recovery.

Between 160 and 250 scans was normally acquired depending on the sample. All ¹³C and ²⁹Si measurements were carried out using SPINAL64 composite-pulse proton decoupling [3] with an rf field between 70 and 80 kHz. ¹H spectra were obtained with a background suppression pulse sequence described in Ref.[4]. The reported chemical shifts for all three nuclei were referenced to tetramethylsilane (TMS).

Electrochemical measurements on composite electrolytes

Electrolytes (11.5 mm diameter, 500 µm thicknesses) were sandwiched between two lithium electrodes in an in-house designed stainless steel cell placed in a glass compartment inside the Ar-filled glovebox. Impedance spectroscopy was measured before and after galvanostatic polarization in a frequency range from 10 MHz to 1 Hz with voltage amplitudes of 0.1 V (Solartron 1260 frequency analyzer). Galvanostatic polarization measurements were performed with Keithley 2604B source meter instrument. All measurements were performed at room temperature.

Zeta potential was determined at room temperature with an electroacoustic spectrometer (DT-1200, Dispersion Technology, Inc., Quantachrome). The electroacoustic sensor measured the magnitude and phase of the so-called Colloid Vibration Current (CVI) at 3 MHz in 1 vol % dispersions of crushed monoliths.

References

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0.4

 p/p_0

1.0







Figure S1. a) SEM micrograph of monolithic Al_2O_3 , b) Nitrogen sorption isotherm of monolithic Al_2O_3 together with the corresponding mesopore size distribution obtained from the adsorption branch by the Barret-Joyner-Hallenda (BJH) method (inset), c) TEM micrograph of crushed monoAl₂O₃.



Figure S2. Bloch decay ²⁹Si {¹H} collected with delay time of 300s.



Figure S3. IR spectroscopy of monoSiO₂ and monoSiO₂– $(CH_2)_3$ -N⁺ $(CH_3)_3Cl^-$ revealing an Si-OH stretching band.



Figure S4. Nitrogen sorption isotherm of $MONOSiO_2-(CH_2)_3-N^+(CH_3)_3Cl^-$ together with the corresponding mesopore size distribution obtained from the adsorption branch by the Barret-Joyner-Hallenda (BJH) method.



Figure S5. Galvanostatic polarization of surface functionalized monoSiO₂ infiltrated with 1 M LiTf/PEGDME-150: a) monoSiO₂-(CH₃)₃, b) monoSiO₂-(CH₂)₃-SO₃H, c) monoSiO₂-(CH₂)₃-N⁺(CH₃)₃Cl⁻, d) monoSiO₂-(CH₂)₃-NH₂. Nyquist plots for monoSiO₂: (1 M LiTf/PEGDME-150) before galvanostatic polarization (black) and after galvanostatic polarization (blue) are shown in the insets.



Figure S6. Room temperature ¹H MAS of mono SiO₂ heated at 300 °C.

	Weight Loss (100 to 800 °C)	Estimated weight loss for functional group
monoSiO ₂	1.69%	_
monoSiO₂-Si-(CH₃)₃	2.68%	2.3%
monoSiO ₂ -(CH ₂) ₃ -SO ₃ H	10.1%	9.6%
monoSiO ₂ -(CH ₂) ₃ -NH ₂	6.65%	5.4%
monoSiO₂-(CH₂)₃-N⁺(CH₃)₃Cl⁻	10.1%	9.2%

Table S1. Measured TGA weight loss and estimated weight loss for different surface groups grafted on $monoSiO_2$.