

Electronic Supplementary Information

Effect of Nanoconfinement on the Glass Transition Temperature of Ionic Liquids

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Materials

1-butyl-3-methylimidazolium tetrafluoroborate (> 98%) was purchased from Alfa Aesar (Tewksbury, MA) and 1-methyl-3-octylimidazolium tetrafluoroborate (99%) was purchased from TCI Chemicals (Portland, OR).

Aluminum foils (99.0%, annealed, thickness = 300 μm) were purchased from Goodfellow Cambridge limited (Huntingdon, England) and used for the preparation of anodic alumina nanotemplates. Phosphoric acid ($\geq 85\%$ in water), oxalic acid (98%), acetone (99.5%), and perchloric acid (70% in water) were purchased from Sigma Aldrich (St Louis, MO). Chromic acid (10% w/v) was purchased from RICCA Chemical (Arlington, TX). Ethanol (200 proof) was purchased from Decon Labs (King of Prussia, PA).

Fabrication of Porous Alumina Membrane

The aluminum foils were cut into rectangular shape (4 cm \times 5 cm) and degreased in acetone through 1 hour of soaking and 5 min sonication. The degreased aluminum foils were then chemically polished by submerging in 5wt% H_3PO_4 aqueous solution at 30 $^\circ\text{C}$ for 3 hours. The polished foils were rinsed with Milli-Q water intensively and dried with nitrogen gas flow.

Two cleaned pieces of aluminum foils were attached to the two electrodes of DC power supply unit (Tekpower, Montclair, California), one serving as cathode and one as anode. The foil pieces were partially (70% of area) dipped into 0.3 M oxalic acid aqueous solution, which is kept at 5 $^\circ\text{C}$ by circulated cooling water running in the jacket of reaction vessel to induce the first anodization process. A pre-defined voltage was applied according to desired pore size for 20 min to 1 hour. Aluminum foils were then taken out of electrolyte solution, sonicated and rinsed with abundant milli Q water.

The oxide layer formed in first anodization process was removed by soaking the aluminum foil pieces in aqueous mixture containing 6 wt% phosphoric acid and 1.8 wt% chromic acid for 4 hours at 75 $^\circ\text{C}$. Subsequently, the foils were taken out of solution, rinsed and sonicated with abundant milli-Q water for 3 times, with each time lasting at least 5 min.

The resulting aluminum foil from first anodization were used as anodes to continue anodization process in 0.3 M oxalic acid solution at 5 $^\circ\text{C}$ for prolonged period of time to allow cylindrical pores to penetrate along the thickness direction of aluminum foil. This process lasts from 1 day to 14 days depending on desired pore size (therefore applied voltage). After the second anodization process, the aluminum foils were taken out from the oxalic acid solution and sonicated in milli-Q water for 5 min before being dipped into an equal volume mixture of ethanol and 70% perchloric acid solution. A voltage around 5 V higher

than anodization voltage was applied until porous alumina membrane macroscopically detached from aluminum substrate. The detached alumina porous membranes were rinsed and sonicated in abundant milli Q water and dried in vacuum over (-30 inHg) overnight before infiltration of ILs.

IL Infiltration into Porous Alumina Membrane

The infiltration of IL through porous alumina membrane was achieved by applying pressure. As illustrated in Figure S1, a glass pipe with inner diameter of 7 mm with both end open was pressed onto a piece of porous alumina membrane with good contact between membrane and the wider end of glass pipe. About 100 μL of IL was then injected through the narrower end of glass pipe to wet the entire porous membrane surface enclosed by glass pipe. Dry nitrogen gas was then pressured into glass pipe from narrower end to force the IL to pass through the porous structure of alumina membrane. A persistent pressure of 90 KPa was typically applied for 1 hour to allow full infiltration of pores, evidenced by wetting of IL on the other side of alumina membrane at the center. The whole process was performed in chamber protected by dry nitrogen gas to ensure humidity effects are minimized.

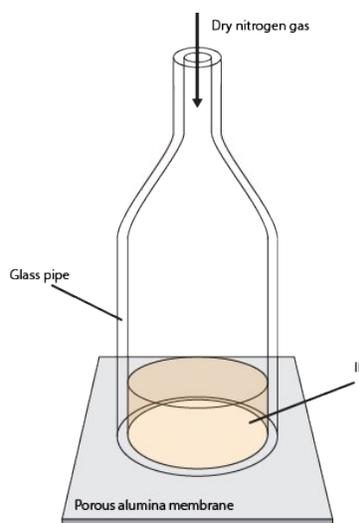


Figure S1. Illustration of mechanism of IL infiltration through porous alumina membrane.

The circular area of IL-infiltrated porous alumina membrane was then carefully broken off from whole piece of membrane and gently wiped with methanol-soaked lint-free paper to remove excess IL on the membrane surface. The infiltrated membranes were further dehydrated in vacuum oven (-30 inHg) prior to DSC measurements.

DSC Measurements

Prior to characterization of samples, baseline was calibrated for empty cell (30 mL/min nitrogen purging flow). Heat flow and temperature were calibrated with indium standard. Subsequently, aluminum and sapphire standards were used to calibrate heat capacity of DSC instrument (DSC Q 2000, TA instruments, New Castle, DE). Approximately 30 mg of IL infiltrated porous alumina membrane pieces were stacked in Hermetic pan and sealed in chamber protected by dry nitrogen gas. Liquid nitrogen was used as coolant of DSC cell and an empty pan was used as reference.

Modulated DSC measurements were performed from $-140\text{ }^{\circ}\text{C}$ to $20\text{ }^{\circ}\text{C}$. A sinusoidal temperature oscillation was coupled with linear increase of temperature, with a modulation oscillation amplitude of $\pm 0.50\text{ }^{\circ}\text{C}$ over characteristic period of 100 s. Linear heating rate was set at $2\text{ }^{\circ}\text{C}/\text{min}$.

Reverse heat flow was decoupled from irreversible heat flow using Universal analysis software (TA instruments) and DSC data was further analyzed using Origin Pro 9.