Supporting Information

Ion Transport in Gel and Gel-Liquid Systems for LiClO$_4$-doped PMMA at the Meso- and Nanoscales

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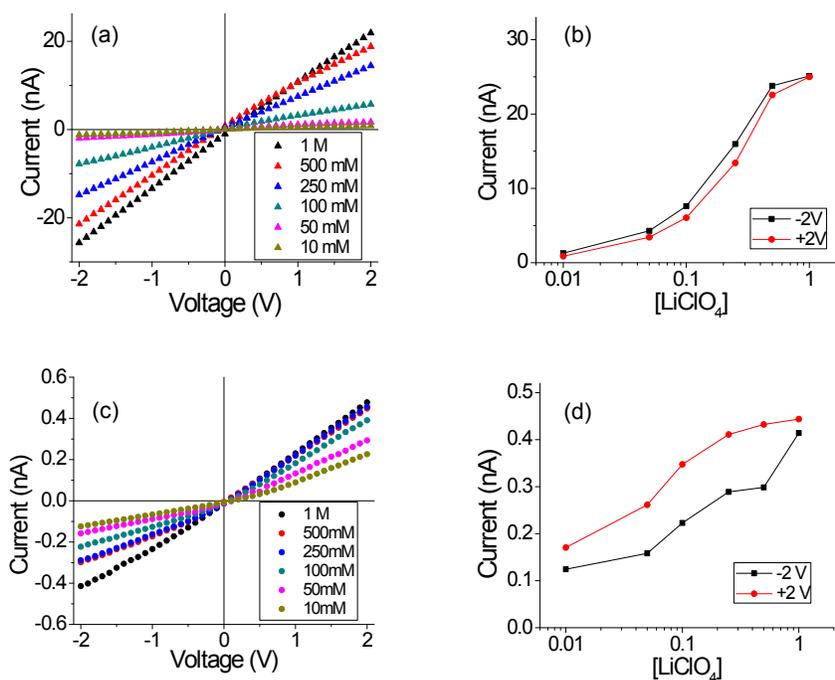
Figure S1. Measurements through empty pores. Current voltage (I-V) measurements and ion current values at +/- 2V over a range of concentrations in LiClO$_4$/PC (1 M -10mM) for a cylindrical (a,b) pore of 640nm in diameter, and a conical (c,d) pore with a base side and tip side of 808nm and 18nm, respectively. These measurements are representative of those taken as a control before samples were drop-cast with PMMA gel.
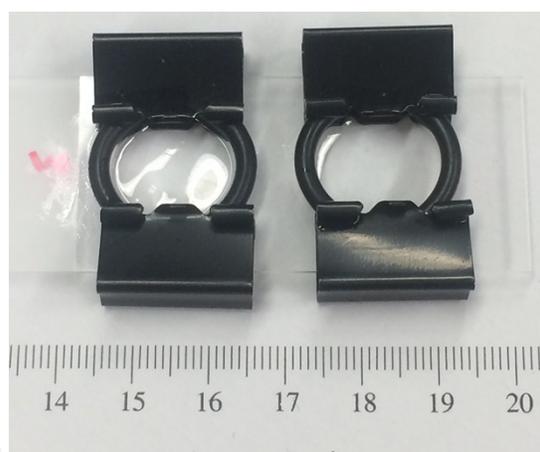
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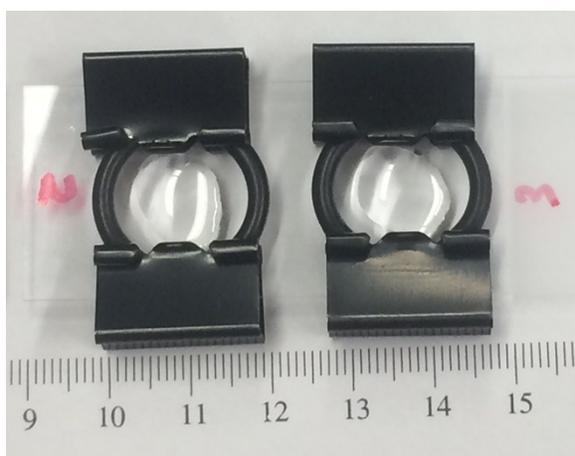
Figure S2 Photographic images of the a) gel-deposited membrane, as well as (b, c) a glass slide upon which two samples of gel have been placed. The gel shown in (b) was exposed to few drops of propylene carbonate for 15 min. The progression from b) to c) demonstrates how the gel can spread due to plasticizing with the propylene carbonate as the gel fills the constraining O-ring. No significant loss of the gel has been observed. The red numbers on the glass slide indicate the percent composition PMMA: '2' marks 25% (w/w) and '3' marks 30%.
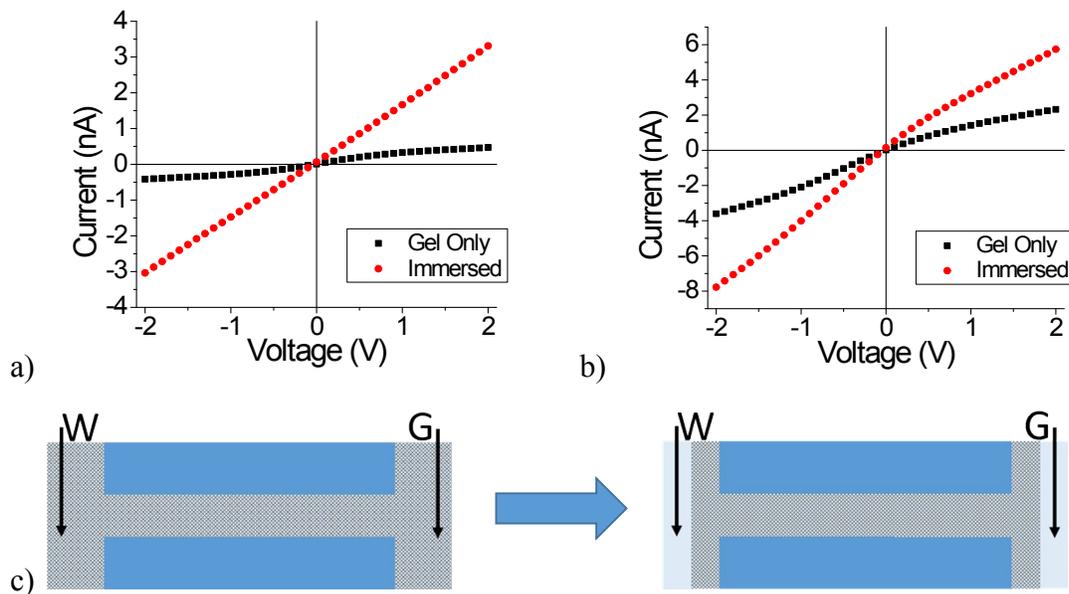
Figure S3. Current-voltage curves through two cylindrical pores filled with PMMA gel doped with 100 mM $LiClO_4$. a) Data from a 330nm in diameter pore; b) data from the 640nm in diameter pore reported in the main manuscript (Fig. 2). Black squares indicate measurements performed with two electrodes placed in the gel on both sides of the membrane; no liquid electrolyte was present. Red circles show data obtained after placing the same pores in contact with a 100mM $LiClO_4$ solution in propylene carbonate. Figure S3c shows the different states which were measured.
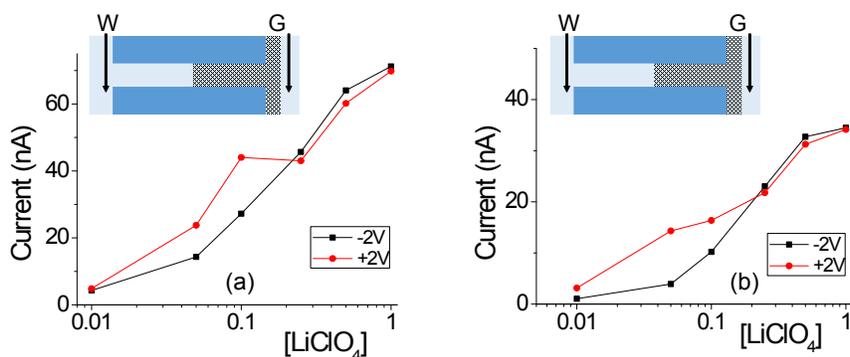
Figure S4. Ion current at +/- 2V for two cylindrical samples which have been deposited with gel on one side only: a) 1100nm in diameter pore with doped gel, b) 790nm in diameter pore with blank (undoped) gel. The doped PMMA gel in (a) contained 100mM $LiClO_4$. Salt concentration in the liquid electrolyte was changed between 10 mM and 1M. Ion current rectification was observed for both samples at lower salt concentrations in the liquid; rectification degrees were higher in the pore containing an undoped gel.
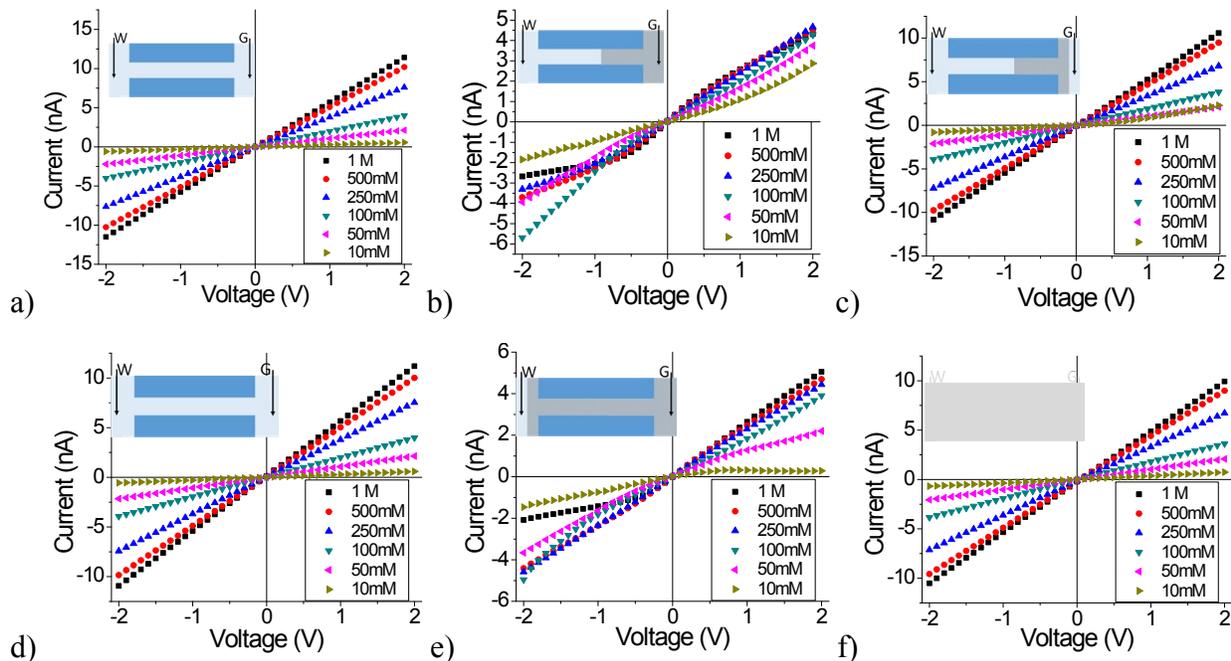
**Figure S5**. Current-voltage curves through single cylindrical pores with opening of (a-c) 410 nm, and (d-f) 420 nm. The 410 nm pore was subjected to one-sided gel deposition; the gel was doped with 100 mM LiClO$_4$ in PC. The 420 nm pore was filled with the gel entirely, the gel was also doped with 100 mM LiClO$_4$. Each pore was studied in three configurations, as shown by the insets: 1) clear - before deposition, 2) in the GLI mode, where one electrode was placed in the gel, and 3) when both sides of the pores were in contact with liquid electrolyte. We see the reduced ionic current in both samples in the GLI experiment (b,e) as opposed to the immersed case (c,f) as well as the rectification feature recur in the double-sided sample, which we attributed to the asymmetric conductive regions of liquid and gel based on PMMA structure having ionic selectivity.
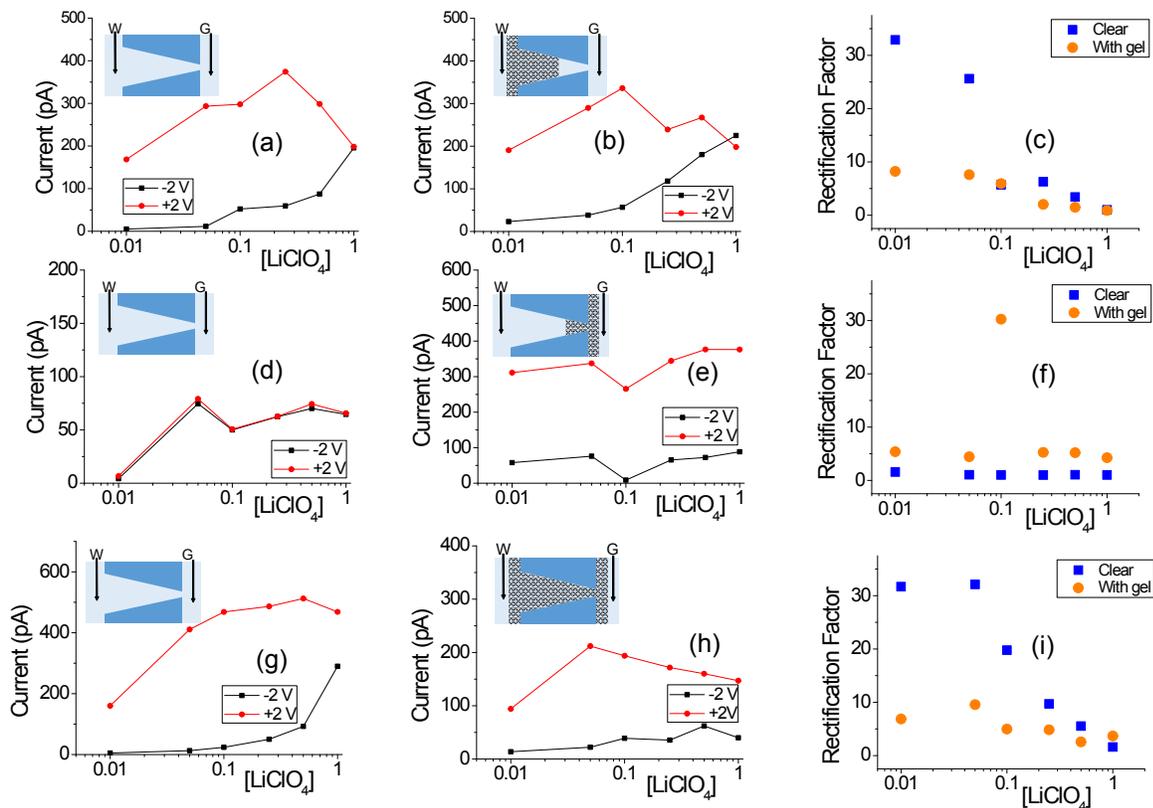
Figure S6. Data from additional samples of three different gel configurations in conical pores with base/tip openings of: (a-c) 1280nm/15nm, (d-f) 415nm/17nm, and (g-i) 570nm/28nm. The placement of the gel is shown in the insets of panels b, e, h. The base configuration for the gel has lower rectification, the tip placement enhances rectification, and the full infiltration also inhibits rectification.
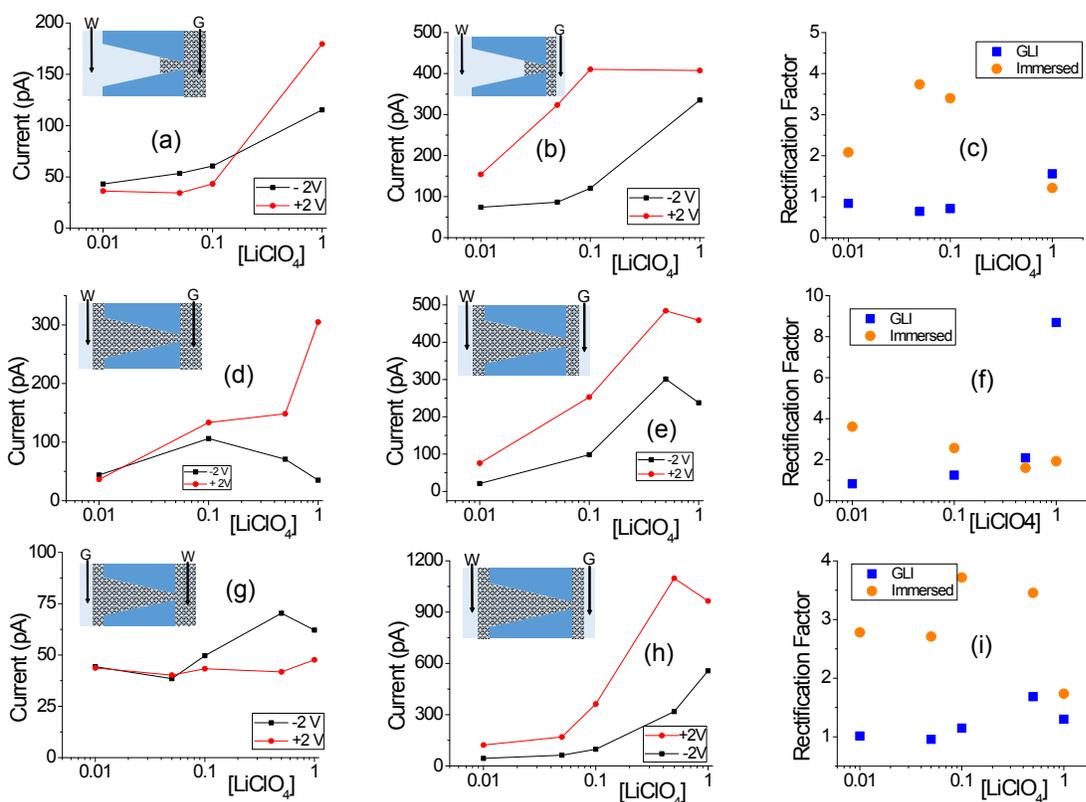
Figure S7. Experiments with conical nanopores subjected to single-sided and double-sided gel casting in the GLI configuration (one electrode placed in the gel, the other one in the liquid electrolyte) and in contact with liquid on both sides of the membrane, as indicated in the insets. Three different conical nanopores were investigated (base/tip opening): (a-c) 550nm/29nm, (d-f) 1060nm/11nm, (g-i) 1470nm/30nm. The sample with gel placed on the tip opening (a-c) exhibited a nearly ohmic behavior at lower salt concentrations. Note that the conical nanopore in (g) was studied in the reversed electrolyte configuration (see the inset) and still exhibited higher currents when anions move from the tip towards the base side. The reverse orientation was used to demonstrate that pore geometry was the dominating effect determining rectification. This is shown by rectification favoring negative voltages with the tip facing the working electrode, which is the analog to the aqueous case of inverse orientation which favors positive voltages. Rectification factor for i) is calculated by $|I_{-2V}/I_{+2V}|$; rectification in c and f was calculated as $|I_{+2V}/I_{-2V}|$.
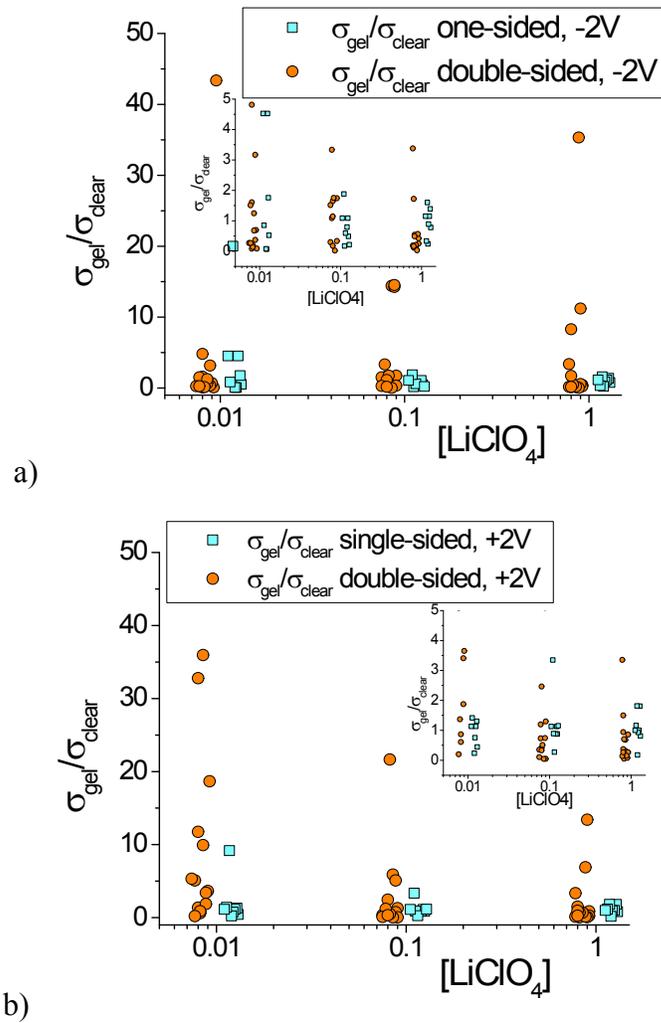
Figure S8. Conductivities of conical nanopores at three benchmark concentrations of $LiClO_4$ in the bulk liquid electrolyte for (a) negative and (b) positive polarities in clear and immersed gel cases. While a majority of samples report lower conductivities for gel-deposited pore systems at both polarities (15 out of 24), there are cases where the conductivity after gel deposition is significantly higher than the open pore. This can be attributed to complications which arise from the rectification of ionic current, barring more quantitative analysis regarding trends. The data jitter is to help visualize the number of samples. All measurements were made in 1 M, 100mM and 10mM $LiClO_4$/PC. The inset show details of the graphs for lower magnitudes of conductivity ratios.