Supporting Information

Experimental

Poly(4-styrenesulfonic acid) lithium salt solution ($PSS^-:Li^+$, M_w ~75,000, 30 wt. % in H_2O), Poly(4-styrenesulfonic acid) sodium salt solution ($PSS^-:Na^+$, M_w ~70,000, 30 wt. % in H_2O), and poly(4-styrenesulfonic acid) solution ($PSS^-:Li^+$, M_w ~75,000, 18 wt. % in H_2O) were purchased form Sigma-Aldrich, and were used as received. The $PSS^-:Li^+$, $PSS^-:Na^+$, and $PSS^-:H^+$ membranes were prepared using an economical solution-based method as protected in our patents.[19,20] The typical thickness of the membrane is ~0.1 mm, and large pieces of membranes (*e.g.*, 10 cm × 6 cm as shown in Fig. 2a) were prepared. The large pieces were then cut into 1.0-cm^2-area disk for device assembly. The SEM (scanning electron microscope) image of the $PSS^-:Li^+$ membrane was obtained using a JEOL JSM-6400F field emission microscope operated in high vacuum.

The graphite/membrane/graphite device was fabricated by sandwiching the 1.0-cm^2-area membrane piece between two graphite pellets. To ensure good contacts, a mechanical pressure of ~ 60 kg/cm^2 was applied to the top graphite pellet by tightening the screw located above it. A YOGOKAWA GS610 source measurement unit was used to collect current-voltage (*IV*) curves of the device. To determine the capacitance and energy storage of the device, the device was first charged under a constant DC voltage of 6 V for 3-5 minutes, and was then discharged under a constant resistance or current. The recorded discharge current *I(t)* or *V(t)* was integrated as function of time *t* for the calculation of charge, energy and capacitance of the device. The above method is relevant to the characterization of polarization-based energy storage such as dielectric electronic polarization and membrane ionic polarization. The AC impedance measurements were carried out using an AUTOLAB workstation in the in the frequency range of 100 kHz to 100 Hz. The AC amplitude was set to 0.01 V, while potential of $\pm$0.7 and $\pm$0.4 V was used respectively to investigate the symmetry of the ionic polarization. All the above measurements were conducted under ambient conditions.