Electronic Supplementary Material (ESI) for Nanoscale

Kinetic factors determining conducting filament formation in solid polymer electrolyte based planar devices

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Fig. S1 shows low-power SEM images showing the effects of gap distances on filament growth morphology and anodic dissolution. The images were taken for Ag/Ag-PEO/Pt and Ag/PEO/Pt devices with three different gap distances of ~2 (a & d), ~1 (b & e), and ~0.5 μm (c & f), respectively, after a forming process with an I_{CC} of 100 nA. The left and right electrodes correspond to Ag and Pt, respectively.

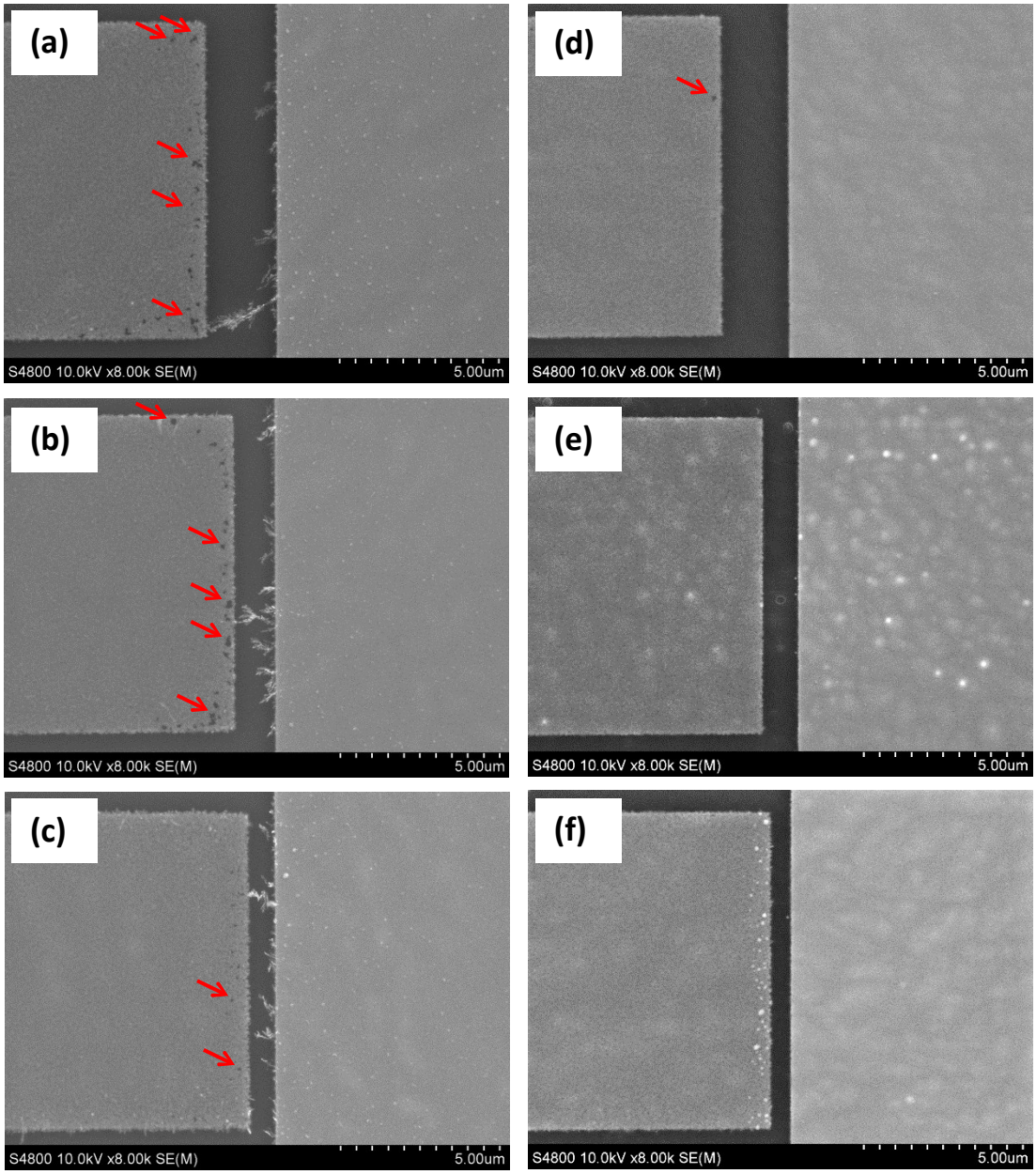

Fig. S1

Fig. S2 shows electric field dependence of the forming time for (a) Ag/Ag-PEO/Pt and (b) Ag/PEO/Pt devices. The different colors correspond to the data obtained from different gap distances. The hopping of Ag^+ ions is a thermally activated process, and the forming time t_f is determined by the bias-dependent activation energy $E_a^{'}$

$$t_f = \frac{1}{v} e^{E_a^{'}/k_B T}, \quad (1)$$

where v is the attempt frequency, k_B is Boltzmann's constant, and T is the absolute temperature. $E_a^{'}$ can be lowered to the first order by a term linearly dependent on the electric field E as $E_a^{'} = E_a - aE$. Here the electric field E is defined by $E = V/d$, where V is the applied voltage and d is the gap distance between electrodes. Equation (1) suggests that the forming time will be reduced exponentially with the electric field, which is consistent with the experimental data, as seen in Fig. S2. This result indicates that the filament growth is facilitated by the electric field in both Ag-PEO and PEO devices, and the ion transport is likely to be the rate-limiting process. The difference in the electric field strength required for the filament growth is attributed to different ionic conductivity in the Ag-PEO and PEO matrices.

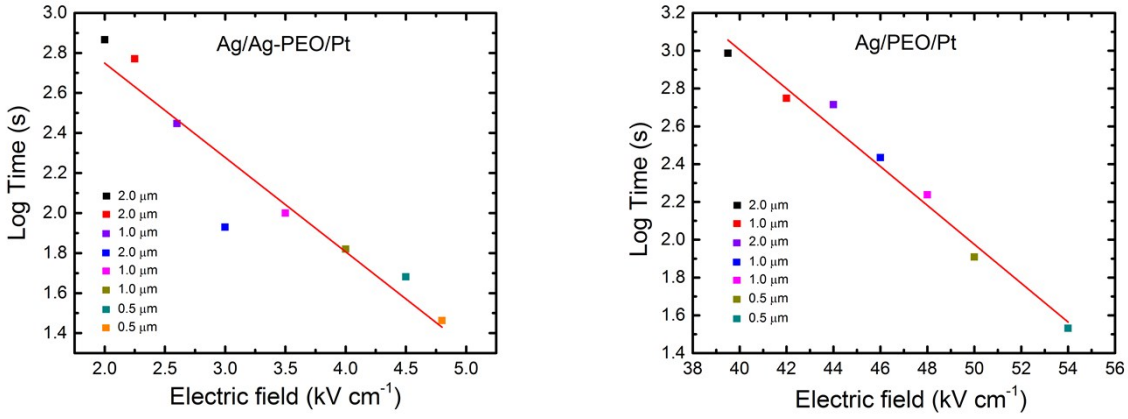

Fig. S2

Fig. S3 shows low-power SEM images of (a) Ag/Ag-PEO/Pt and (b) Ag/PEO/Pt devices taken after forming process with an I_{CC} of 10 μA. The left and right electrodes correspond to Ag and Pt, respectively. The gap distance was fixed to ~0.5 μm for both devices.

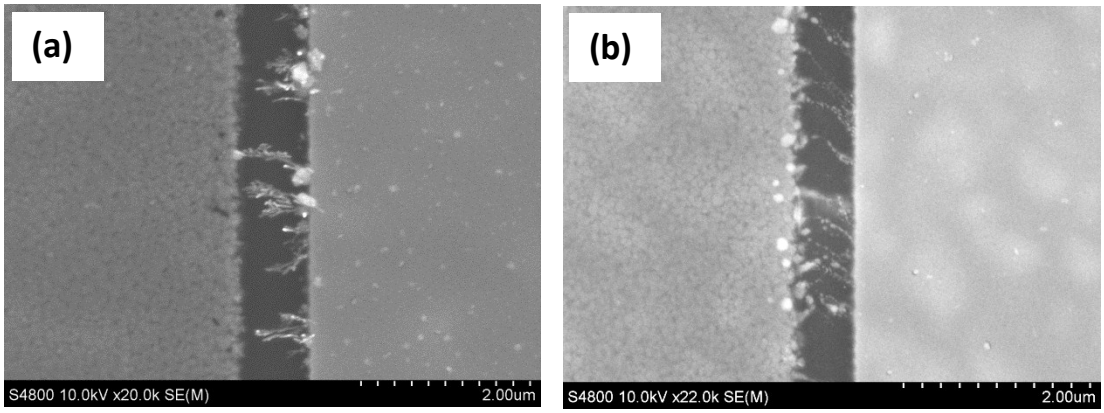

Fig. S3