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Densification and Performance Optimization of NaSICON Solid Electrolytes via Low-Temperature Cold Sintering Process with Sodium Ionic Salts Doping

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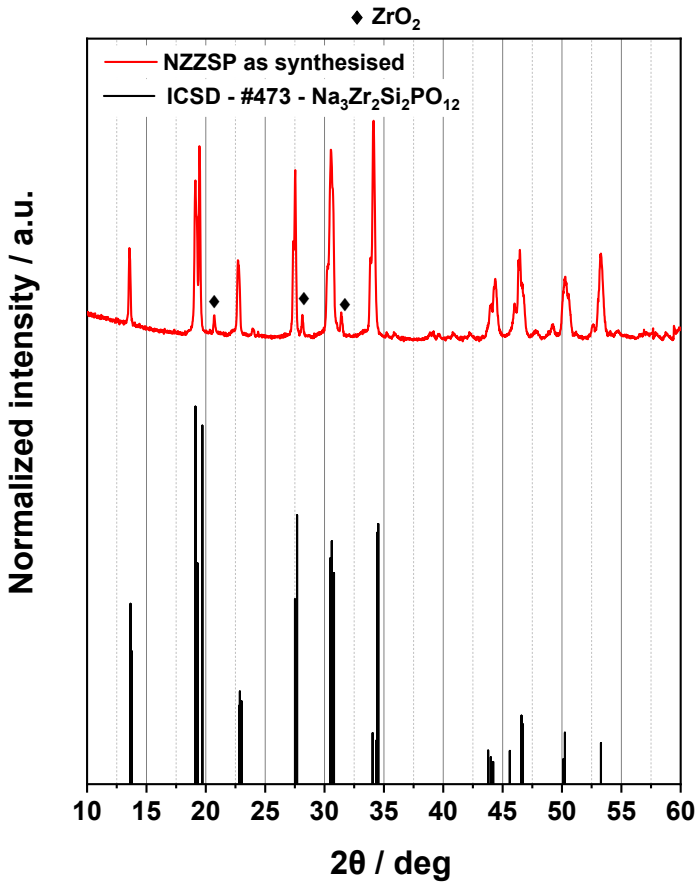

Fig. S1. XRD diffractogram of the NZZSP powder after synthesis at 1000ºC for 4 hours and 1200ºC for 10 hours (red) and XRD pattern of the standard ICSD - #473 $Na_3Zr_2Si_2PO_{12}$

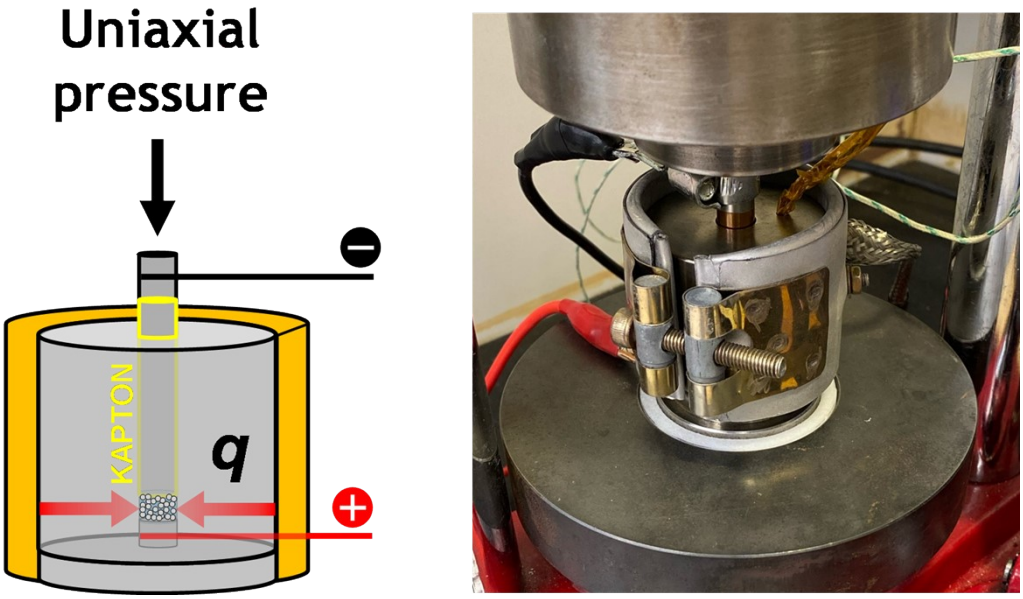

Fig. S2. Set up employed for the *operando* Cold Sintering Process for the production of NZZSP samples in this study.

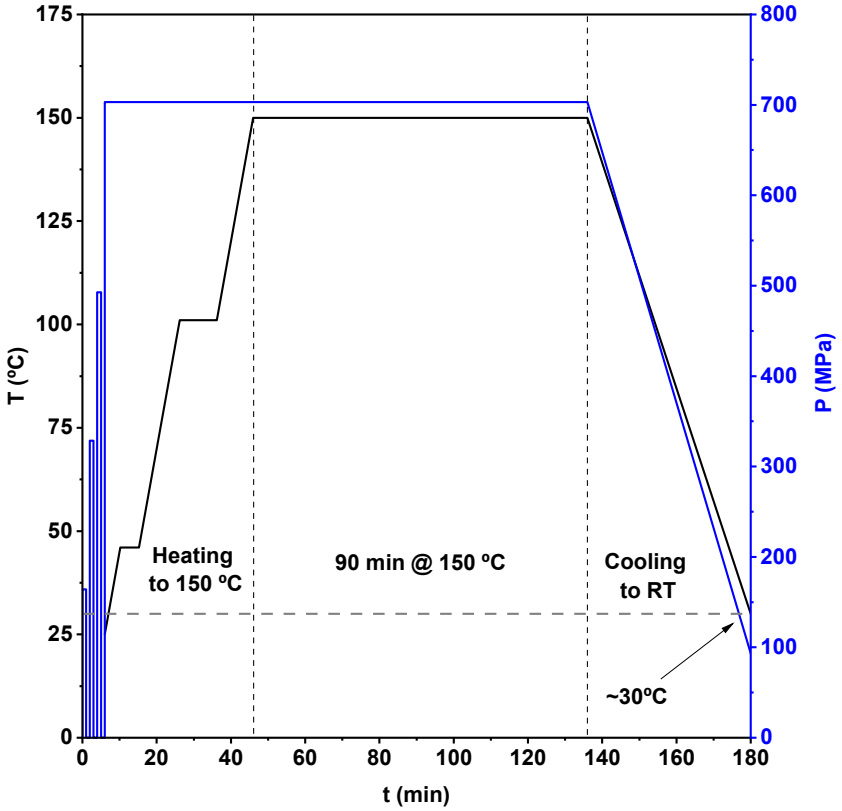

Fig. S3. Pressure (blue) and temperature (black) cycle employed in the CSP.

In the cycle, before starting to heat up to 150 ºC, three consecutive deaerations of 1 minute at 150, 300 and 500 MPa are made to compact the initial powder. After 90 minutes of dwell time at 150 ºC, the heating is turned off and the CSP set up is naturally cooled down to room temperature (~30 ºC). At that point, the cycle is finished, the pressure is removed, and the last EIS measurement is made without pressure.

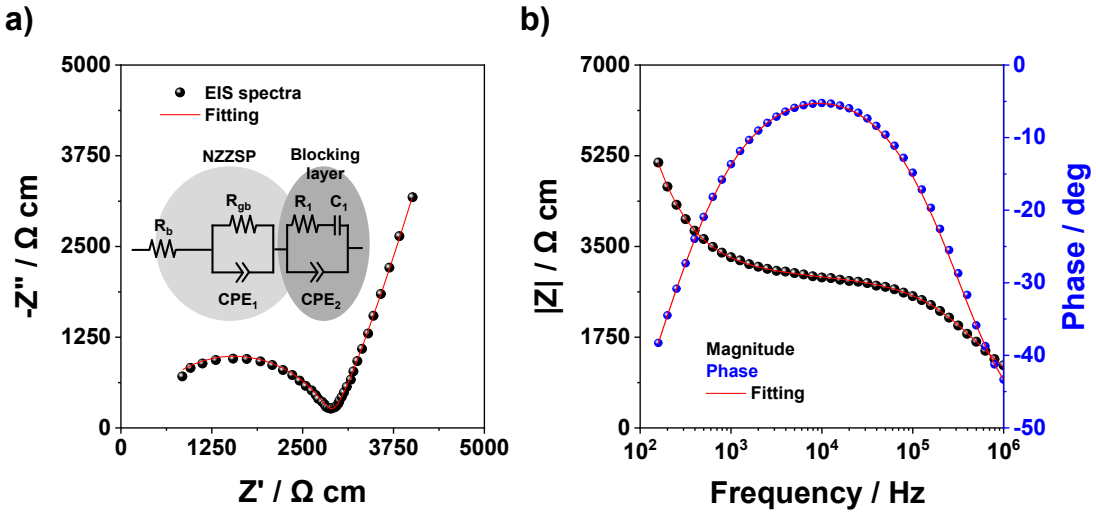

Fig. S4. (a) Nyquist diagram and fitting of a generic EIS spectrum of the NZZSP. The equivalent circuit employed for the fitting is shown in the inset. (b) Bode diagram of the same sample and its fitting.

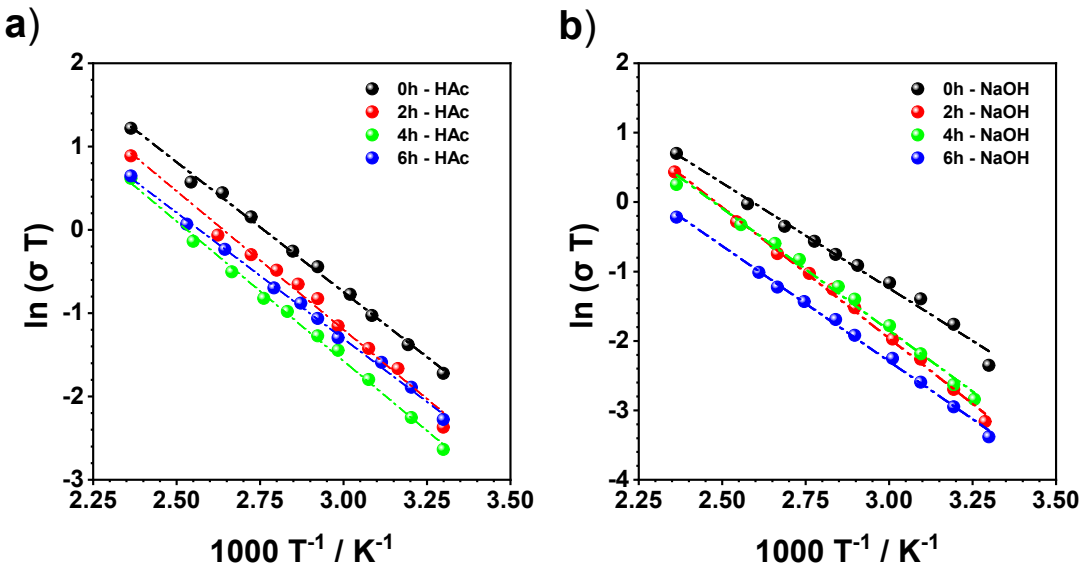

Fig. S5. Arrhenius fitting of one series of EIS data from the cooldown of the CSP for (a) the acetic acid (3M HAc) and (b) the sodium hydroxide (25 mM NaOH) series for the TLP study of the NZZSP.

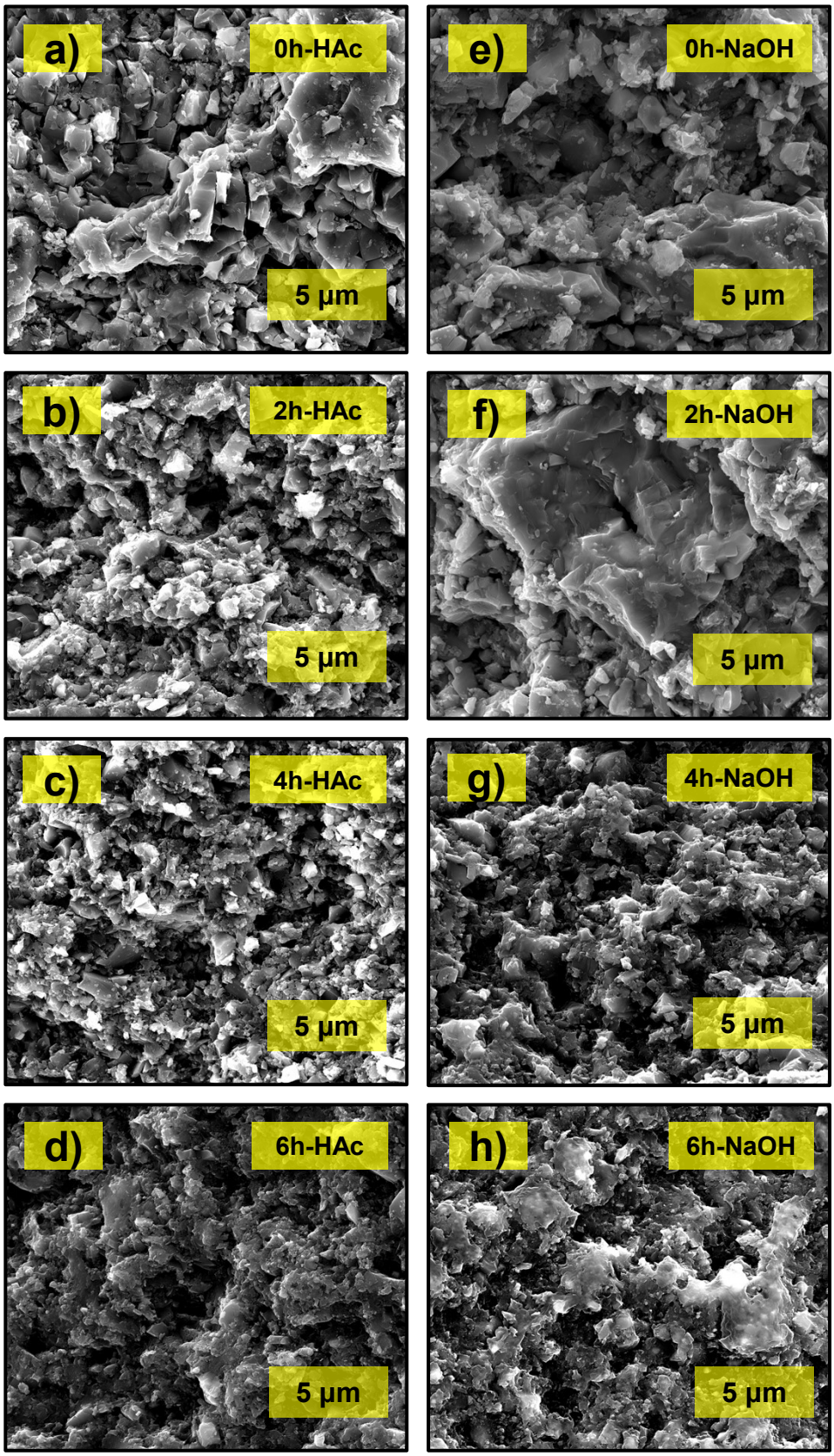

Fig. S6. Cross-section SEM images of NZZSP SSEs cold sintered with powder from 0h, 2h, 4h and 6h milling times for the HAc TLP series (a)-(d) and the NaOH TLP series.

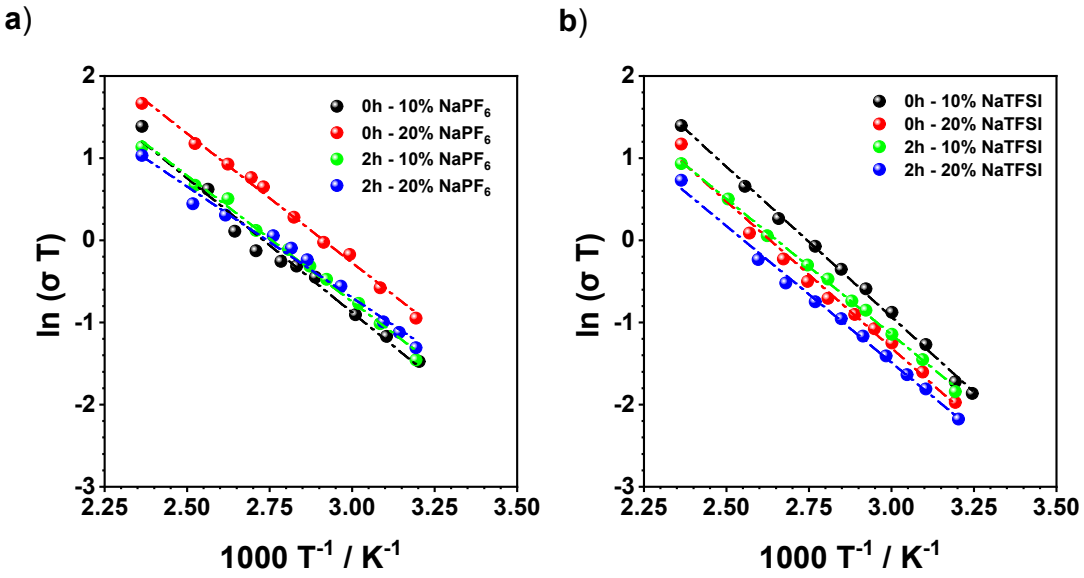

Fig. S7. Arrhenius fitting of one series of EIS data from the cooldown of the CSP for (a) the $NaPF_6$ and (b) the NaTFSI series for the ionic salts doping study of the NZZSP.

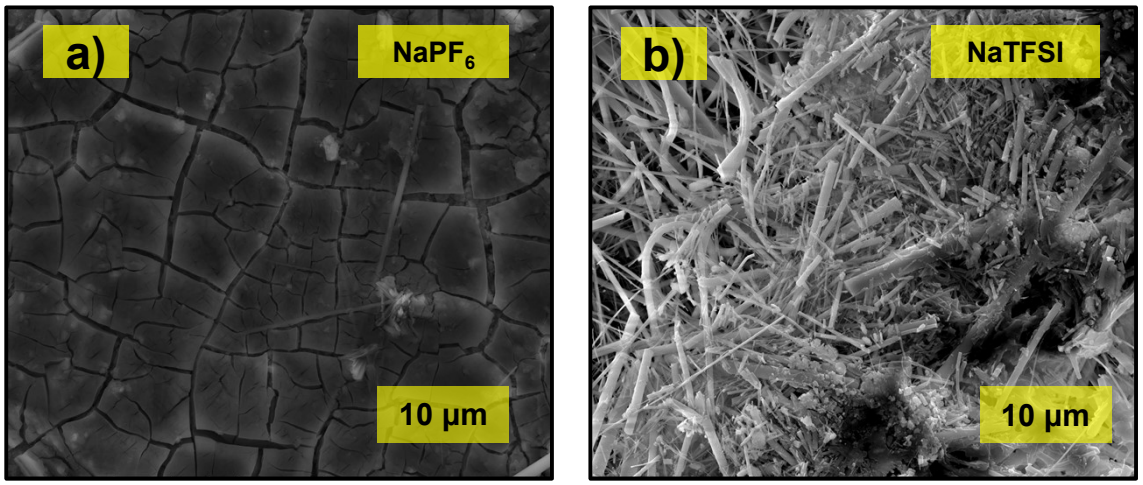

Fig. S8. SEM images of (a) the $NaPF_6$ and (b) the NaTFSI ionic salts deposited on a commercial Whatman glass-fibre filter through a droplet of the acetic acid TLP solutions employed in the doping study of the NZZSP.

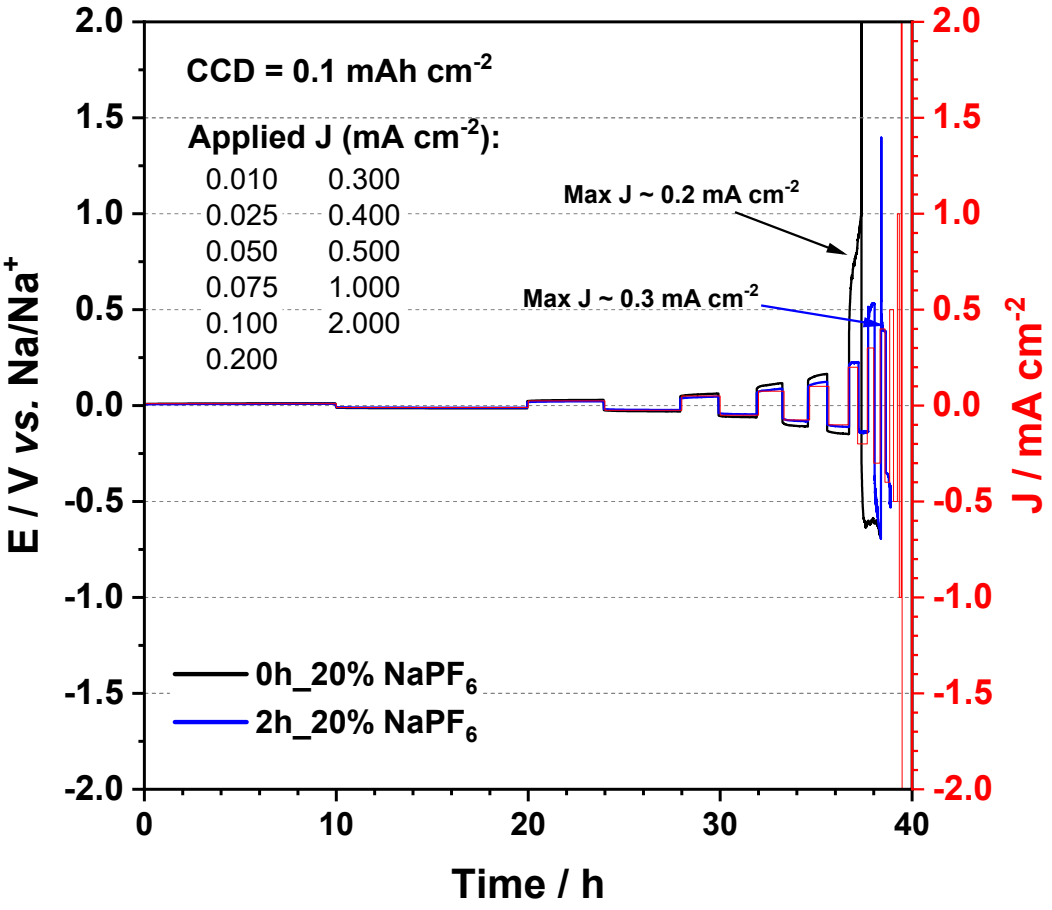

Figure S9. Critical current density characterization of the 0h- and 2h-20% $NaPF_6$ electrolytes under multiple current densities (0.01, 0.025, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2 mA cm^{-2}). A CCD capacity of 0.1 mAh cm^{-2} has been established for the measurement.

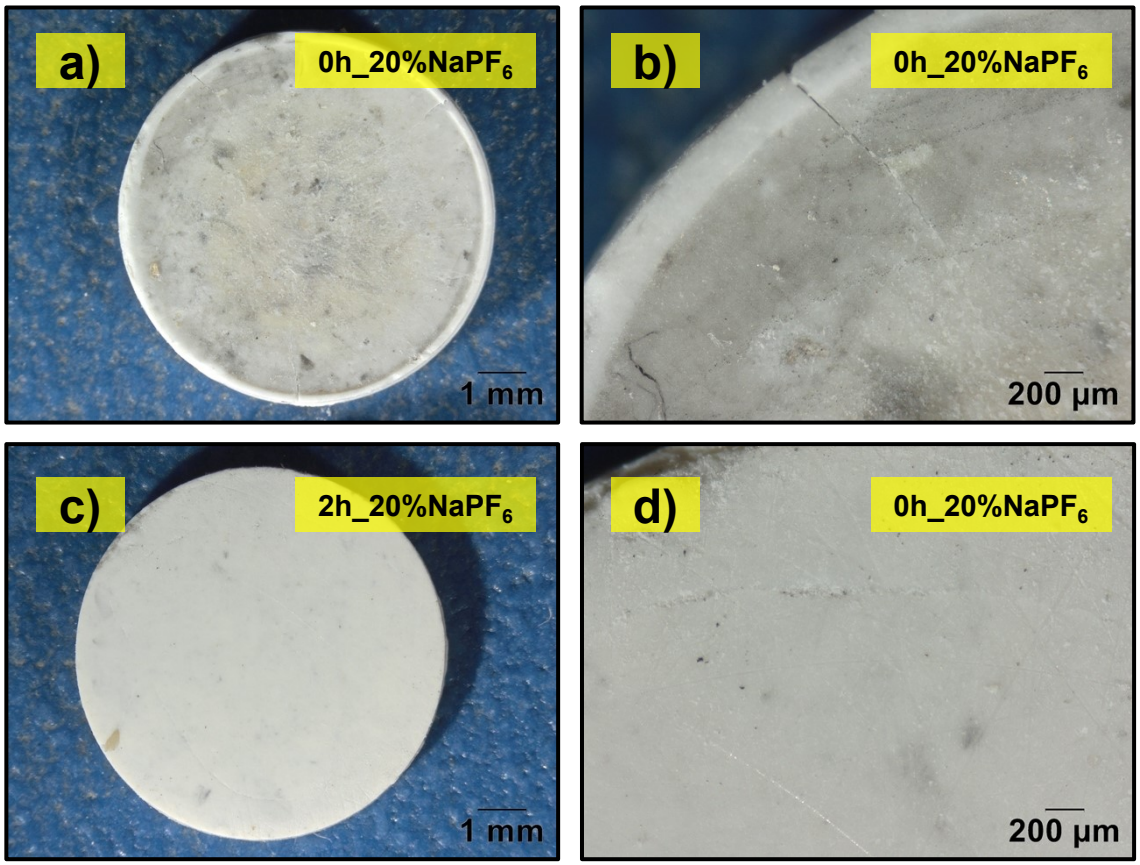

Fig. S10. Optical images of (a) – (b) the 0h_20% $NaPF_6$ sample surface and (c) – (d) the 2h_20% $NaPF_6$ sample surface after cycling in the Na symmetric cell for over 200 and 500 hours respectively. Superficial damage is appreciable in the surface of the 0h_20% $NaPF_6$ sample after being affected by sodium dendrites.