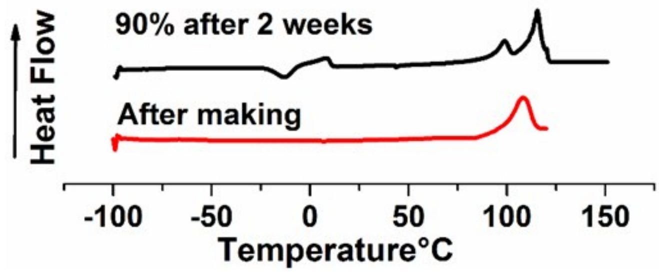


Figure S1. DSC heating trace of fresh 90 mol% and after 2 weeks

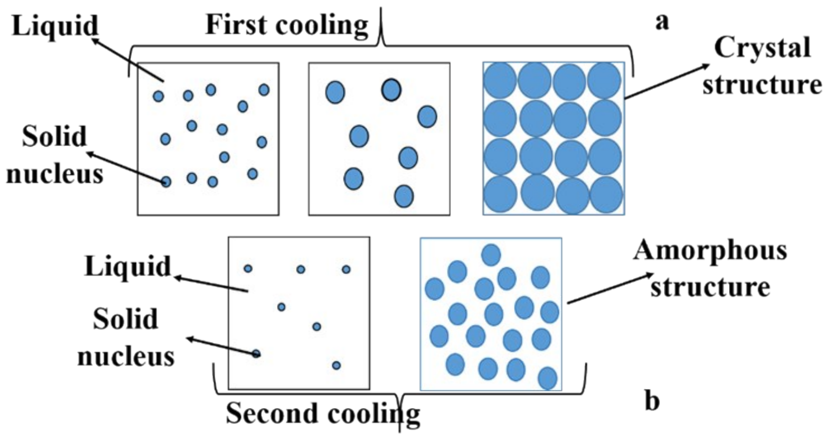


Figure S2. Schematic figure of nucleation and growth

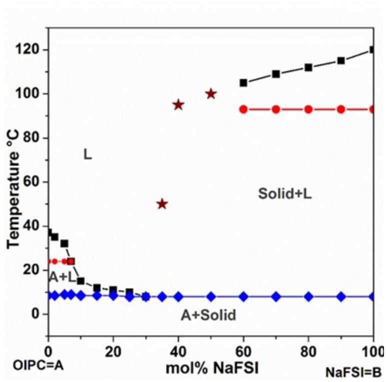


Figure S3. Binary phase diagram of $P_{1i444}$/NaFSI

As mentioned before eutectic transition occurs at 8 ℃ (at the same temperature of solid-solid phase transition) at 30 mol% NaFSI. Below this transition samples solidify into two different solids. 3 regions are evident in the phase diagram:

1- OIPC rich phase:

This region is at the concentrations below 30 mol% in which decreasing melting temperature by increasing the concentration of NaFSI is their common behaviour. At areas between eutectic temperatures and melting temperatures (liquidus line) double phases (liquid and solid) coexist with each other. The solid phase might belongs to OIPC or a new compound between pure OIPC and 30 mol% NaFSI.

2- This region belongs to the composition that their crystallisation is very difficult and methodical annealing forced them to form crystalline phase.

3- Na-salt rich phase:

This region have connection with the highest concentration of NaFSI. At this region liquidus line increases slightly by increasing the Na salt content. At temperatures between eutectic and melting transitions two phases coexist; liquid and solid phases.

Apparently the phase behaviour of these mixtures is very complicated and the existing other compounds at low concentration of NaFSI and also at the range of 40 to 50 mol% is possible.

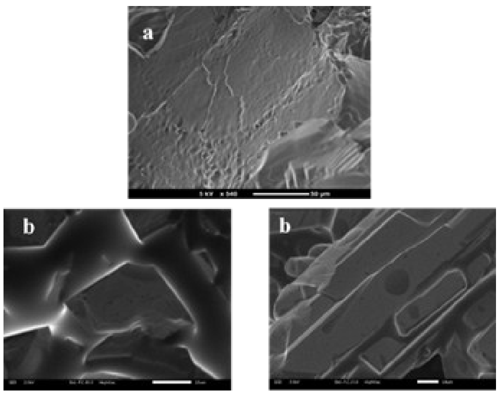


Figure S4. Micrograph images of (a) pure $P_{1i444}$FSI OIPC (b) mixed with 90 mol% NaFSI

SEM images of pure OIPC shows the grain boundaries and the smooth surface that are the typical features of OIPCs.

SEM images of 90 mol% at room temperature shows both liquid and solid phases which is in agreement with the phase diagram and confirmed the existence of eutectic transition below room temperature. From the phase diagram crystalline part of 90 mol% should belong to NaFSI and the liquid part contains enriched Na electrolyte that is responsible for high ionic conductivity of these samples.

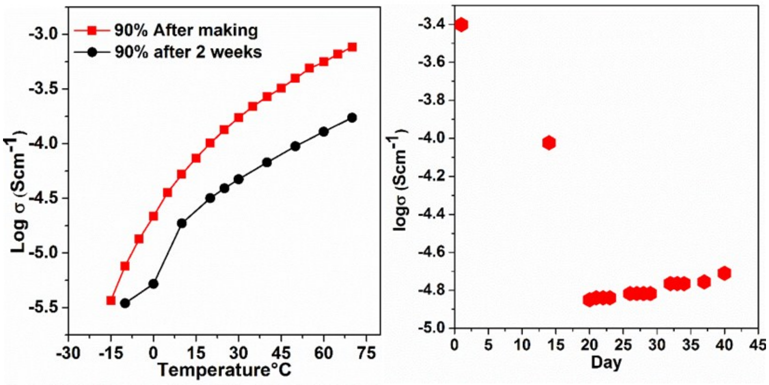


Figure S5. Ionic conductivity of 90 mol% NaFSI/$P_{1i444}$FSI (a) after two weeks, (b) during several days

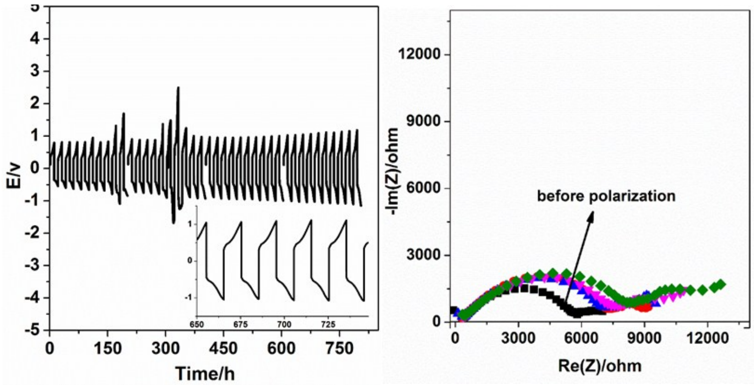


Figure S6. Voltage-time profiles for a Na symmetric cell at 0.1 $mAcm^{-2}$ with 10 minutes intervals for a cell containing 90 mol% NaFSI in $P_{1i444}$FSI electrolyte at 50℃.

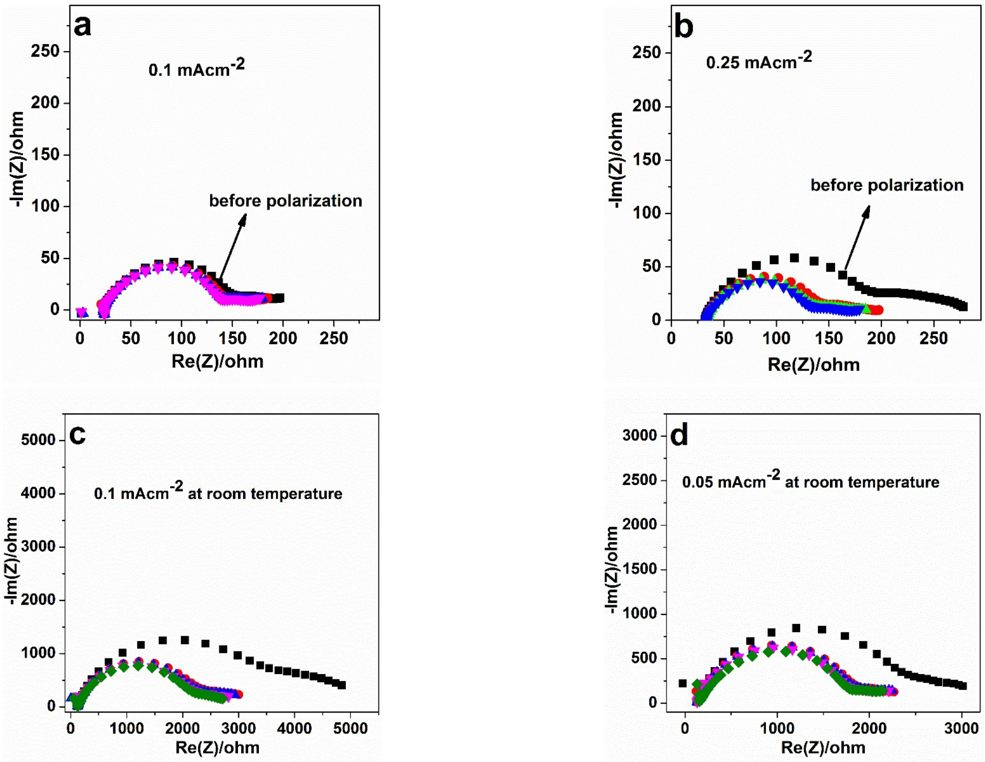


Figure S7. EIS data of 60 mol% $P_{1i444}$FSI/NaFSI a) at 50 C with current density of 0.1 mAcm$^{-2}$, b) at 50 C with current density of 0.25 mAcm$^{-2}$, c) at room temperature with current density of 0.1 mAcm$^{-2}$, d) at room temperature with current density of 0.05 mAcm$^{-2}$

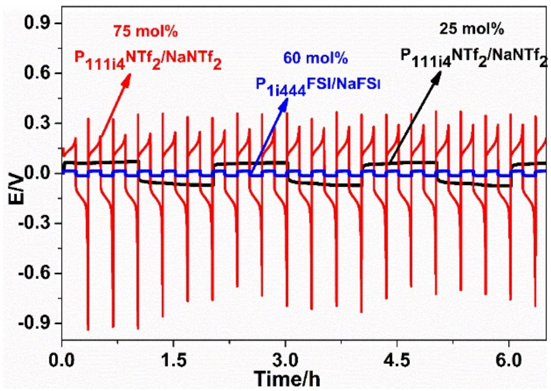


Figure S8. Voltage-time profiles for Na symmetric cells at 0.1 mA.cm$^{-2}$ at 50 °C for different electrolyte compositions

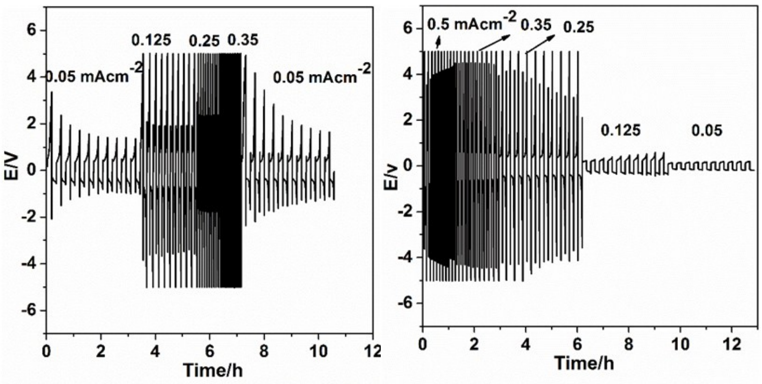


Figure S9. Galvanostatic charge–discharge cycling of a Na|90 mol% NaFSI mixed $P_{1i444}FSI$|Na cell at 25 °C, a) Cycling at different current densities from low 0.1 mA cm$^{-2}$ to high 1 mA cm$^{-2}$, b) Cycling at different current densities from high 1 mA cm$^{-2}$ to low 0.1 mA cm$^{-2}$.