Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

New approach for obtaining ceramic NASICON ($Na_3Zr_2Si_2PO_{12}$) films sintered in situ by a sol-gel method, using spray deposition and Near-Infra Red Sintering

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Supporting Figures

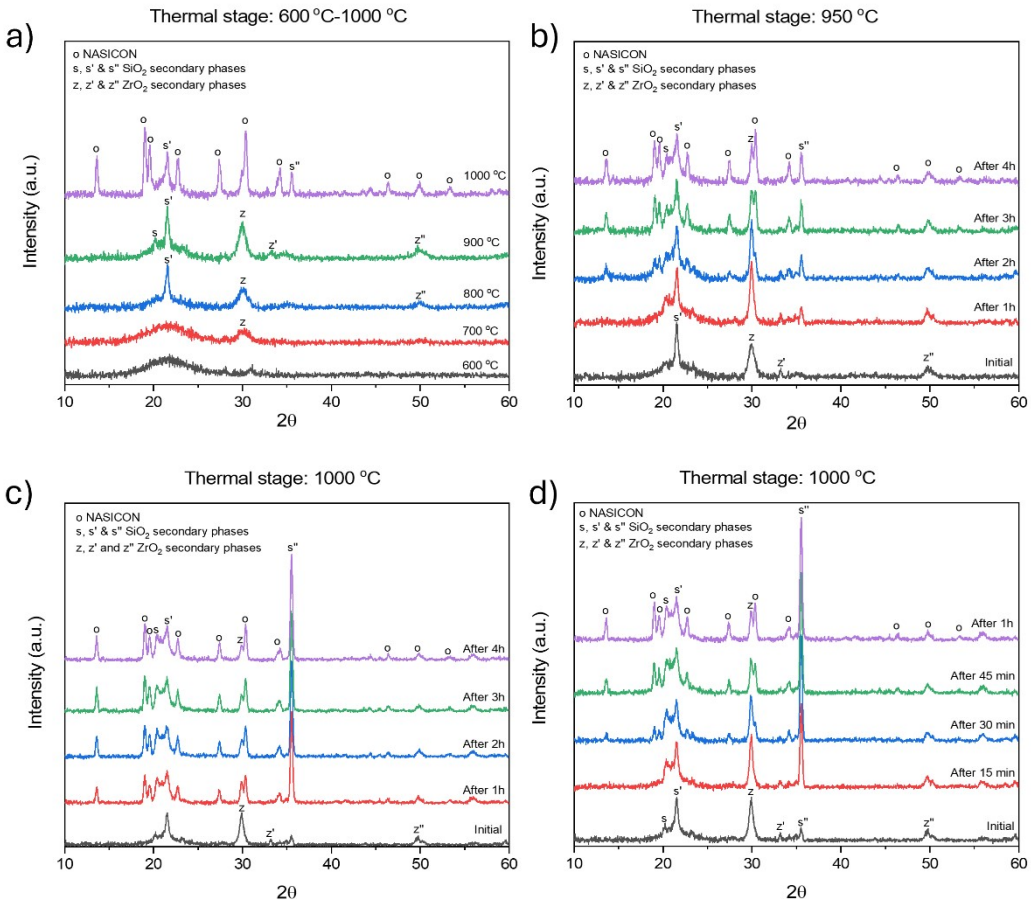

Figure S1.- Thermal stage XRD of NASICON sample sintered: a) between 600-1000 °C, b) at 950 °C (measurement per hour), c) at 1000 °C (measurement per hour), d) at 1000 °C (measurement per 15 min)

Figure S2.- Video of NASICON film NIR sintered

Characterisation Equipment

The crystallinity of the powders and films sintered was analysed by X-Ray Diffraction (Bruker D8 Discover XRD) using Cu Kα radiation source (λ = 1.5406 Å, angle range 2θ = 10−60°). Glancing Incidence XRD (GI-XRD) was measured in a true parallel beam mode using a Goebel mirror optic and axial soller system with incidence angle fixed between 0.5° and 4.5° to control interaction depth. Thermal XRD tests were carried out using a DHS 1100 (Anton-Paar) mounted onto the D8 Discover. For each temperature step samples were heated at a rate of 5°C/min and held for 10 minutes to allow stabilisation. The measurements were undertaken with a point source and polycapillary optic and a 2mm collimator. Thermogravimetric Analysis and Differential Scanning Calorimetry in air (TGA/DSC) was used to analyse the dried sol (Seteram Labsys Evo (STA), temperature range 25-1200 °C). The irradiance spectrum was obtained from a AdPhos NIR Coil Lab LV2 unit. This equipment uses lamps similar to the ones in the adphosNIR® 6 × 6 kW ceramic based NIR machine. To perform the measurement two portable Ocean Optics spectrometers where used, an HR2000+ UV/VIS (range 200-1100 nm) and NIRQUEST256 NIR (range 900- 2500 nm); the input fibre with cosine corrector was positioned 5 cm away and 10 cm above the exit of the lamps to avoid thermal damage and data was collected for each power setting at 1 m/min speed (25 s exposure). UV/visible/NIR spectroscopy (Perkin Elmer UV-Vis-NIR spectrometer) was used to measure the NIR absorbance of the fused silica substrate, and the different films prepared (wavelength range λ = 500-2000 nm). The morphology of the NASICON films (oven and NIR sintered) was analysed by scanning electron microscopy (SEM, JEOL 7800F FEG-SEM). Raman spectroscopy analysis of films was performed with a Renishaw inVia Raman microscope using a laser with an excitation wavelength of 532 nm (~3 mW). 25mm diameter fused silica discs with the spray coated NASICON films on top were masked with platinum and then coated with silver to serve as the contact (Figure S3).

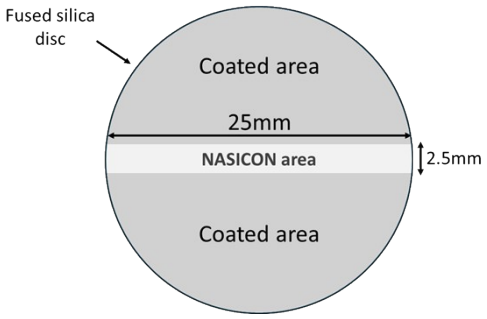

Figure S3.- Plan View of NASICON film on fused silica disc Pt-sputtered and Ag-coated

Ionic resistivity (R) was measured at room temperature and open circuit using a Gamry 620 potentiostat with a frequency between 1Hz and 3MHz at an amplitude of 10mV.

$$\sigma = \frac{t}{A \times R} \quad (1)$$

The ionic conductivity (σ) was calculated using equation 1, with the film thickness (t) estimated by SEM images at 10 microns for both the oven and NIR sintered films. A is the cross-sectional area (film thickness x diameter of disc):

$$A = 10\ \mu m \times 2.5\ cm = 1 \times 10^{-4}\ cm \times 2.5\ cm = 2.5 \times 10^{-4}\ cm^2$$