



## Article

# Spray-Flame Synthesis of NASICON-Type Rhombohedral ( $\alpha$ ) $\text{Li}_{1+x}\text{Y}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ [ $x = 0\text{--}0.2$ ] Solid Electrolytes

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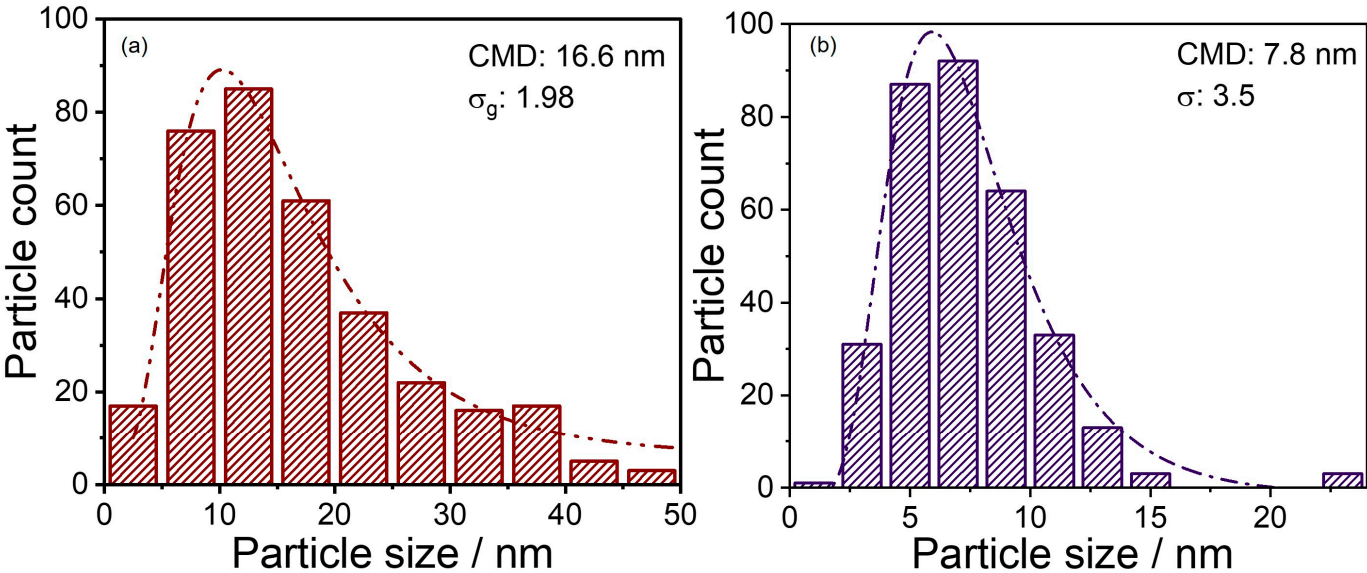
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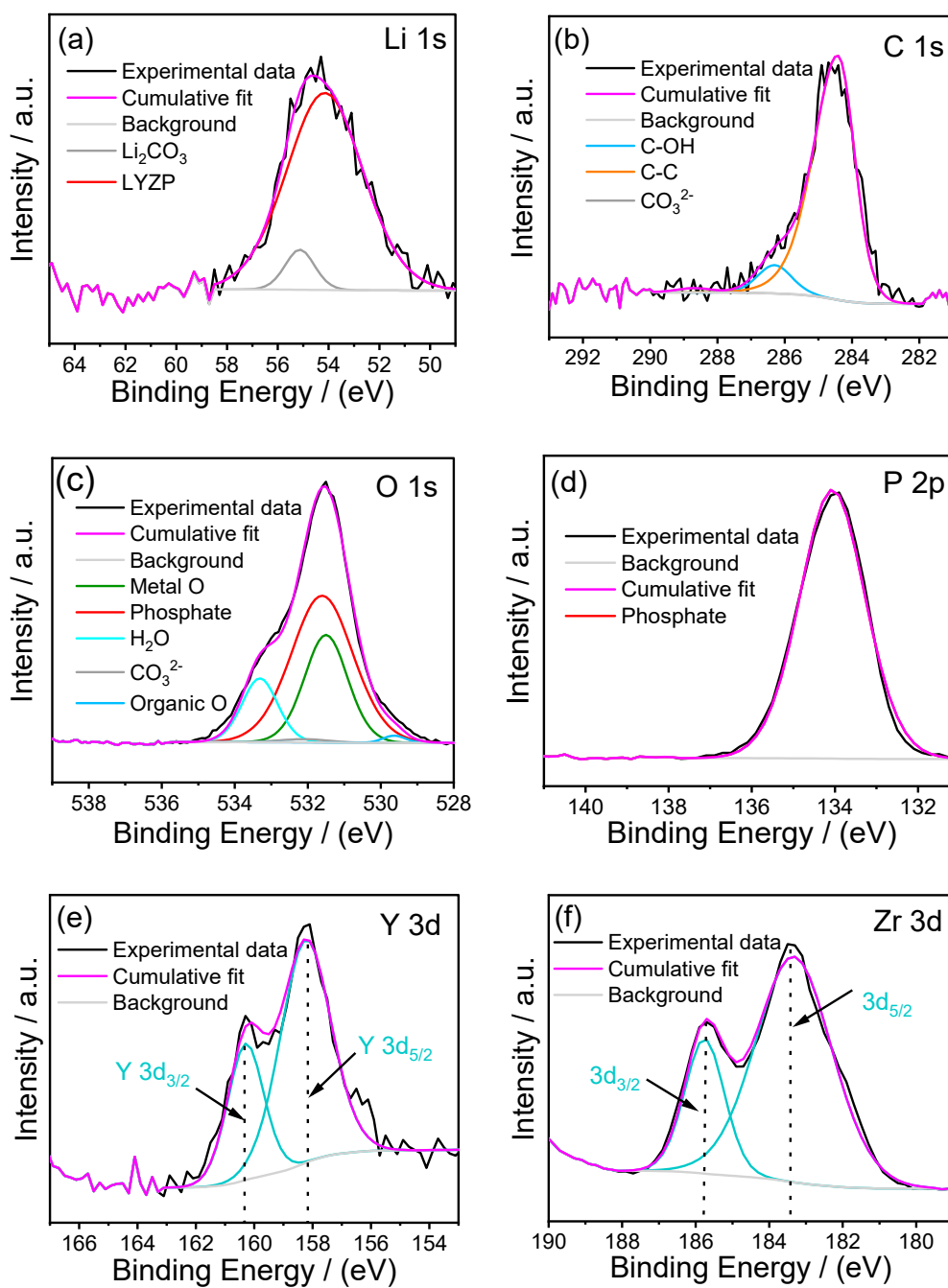
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**Table S1.** Physical properties of solvents and precursors

Chemical Formula	Category	Melting point [°C]	Boiling point [°C]
LiNO <sub>3</sub>	Solute	255	600
Y(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Solute	52	Decomposes at 640
Zr(NO <sub>3</sub> ) <sub>4</sub> (ZN)	Solute	/	Decomposes at 100
Zr <sup>x+</sup> ·xH <sub>3</sub> CCOOH (ZA)	Solute	/	/
Zr(OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub> (ZP)	Solute	661	/
2-Propanol	Solvent	/	82
Propionic acid	Solvent	/	141
Ethanol	Solvent	/	78
2-Ethylhexanoic acid	Solvent	/	217
Acetic acid	Solvent	/	118



**Figure S1.** Particle size distribution of as-synthesized particles from case (LY<sub>0.2</sub>ZP)<sub>PA50</sub> (a) and (LY<sub>0.2</sub>ZP)<sub>EA50</sub> (b) respectively.

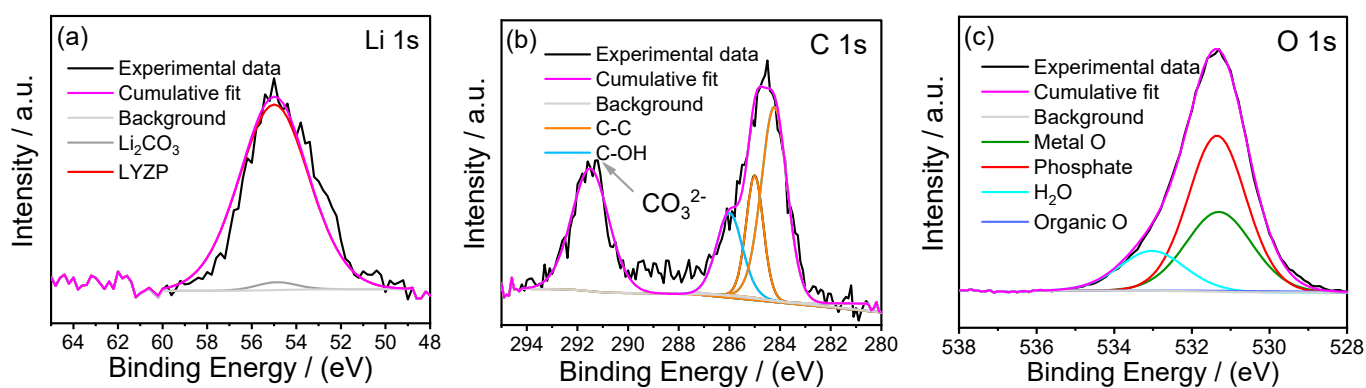


**Figure S2.** Results of XPS measurements of (a) Li 1s. (b) C 1s. (c) O 1s. (d) P 2p. (e) Y 3d. (f) Zr 3d of as-synthesized (LY<sub>0.2</sub>ZP)<sub>PA50</sub>

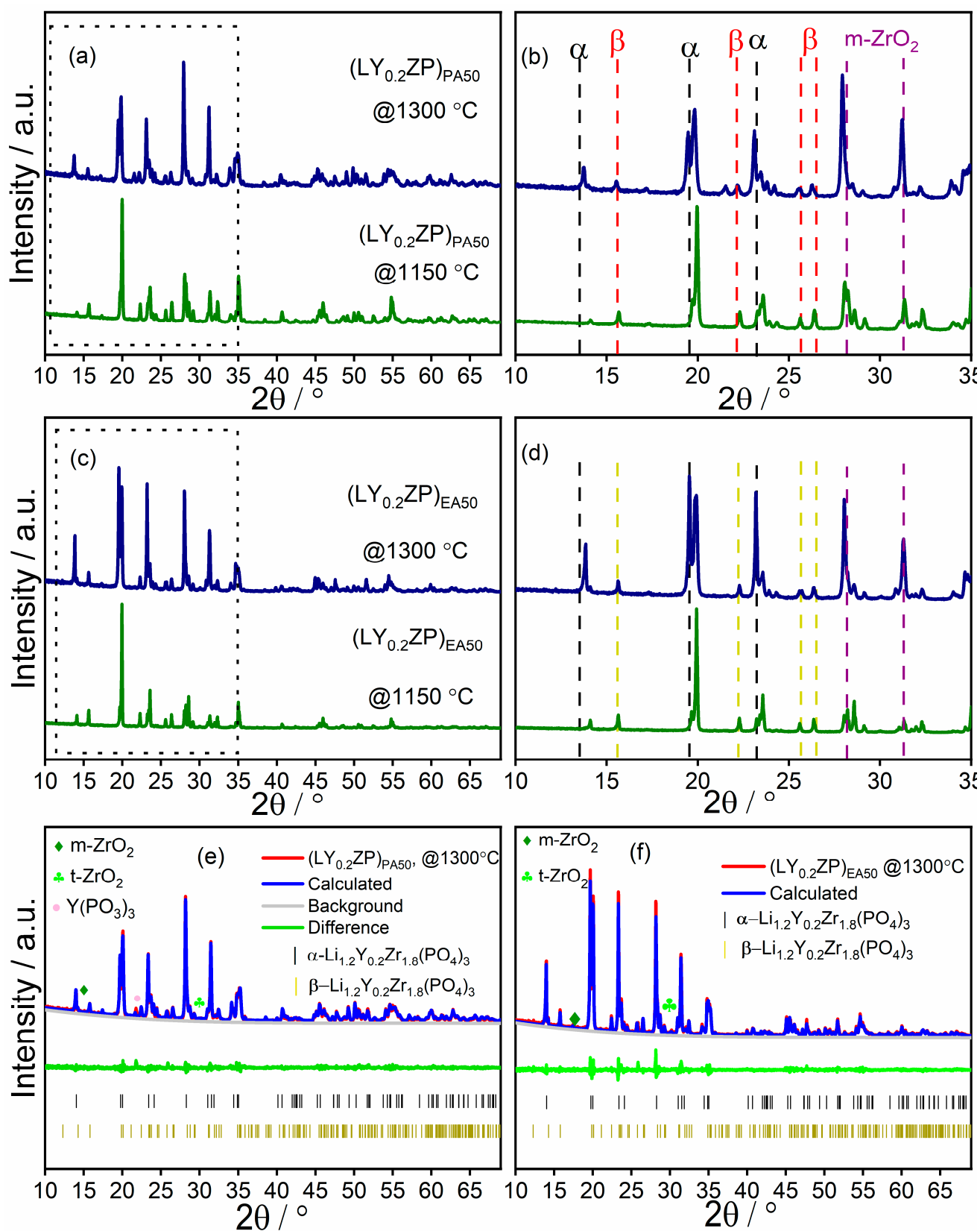
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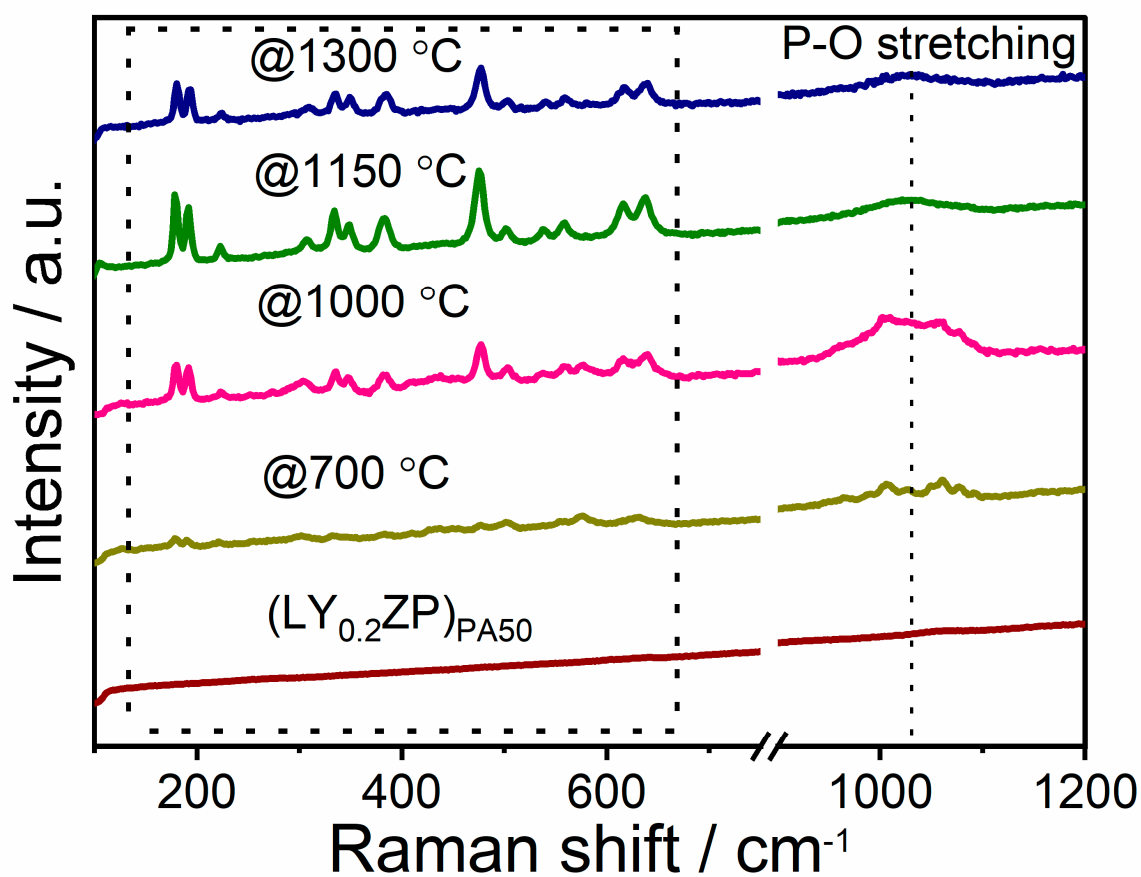
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**Figure S3.** Results of XPS measurements of (a) Li 1s. (b) C 1s. (c) O 1s of as-synthesized  $(LY_{0.2}ZP)_{EA50}$ .

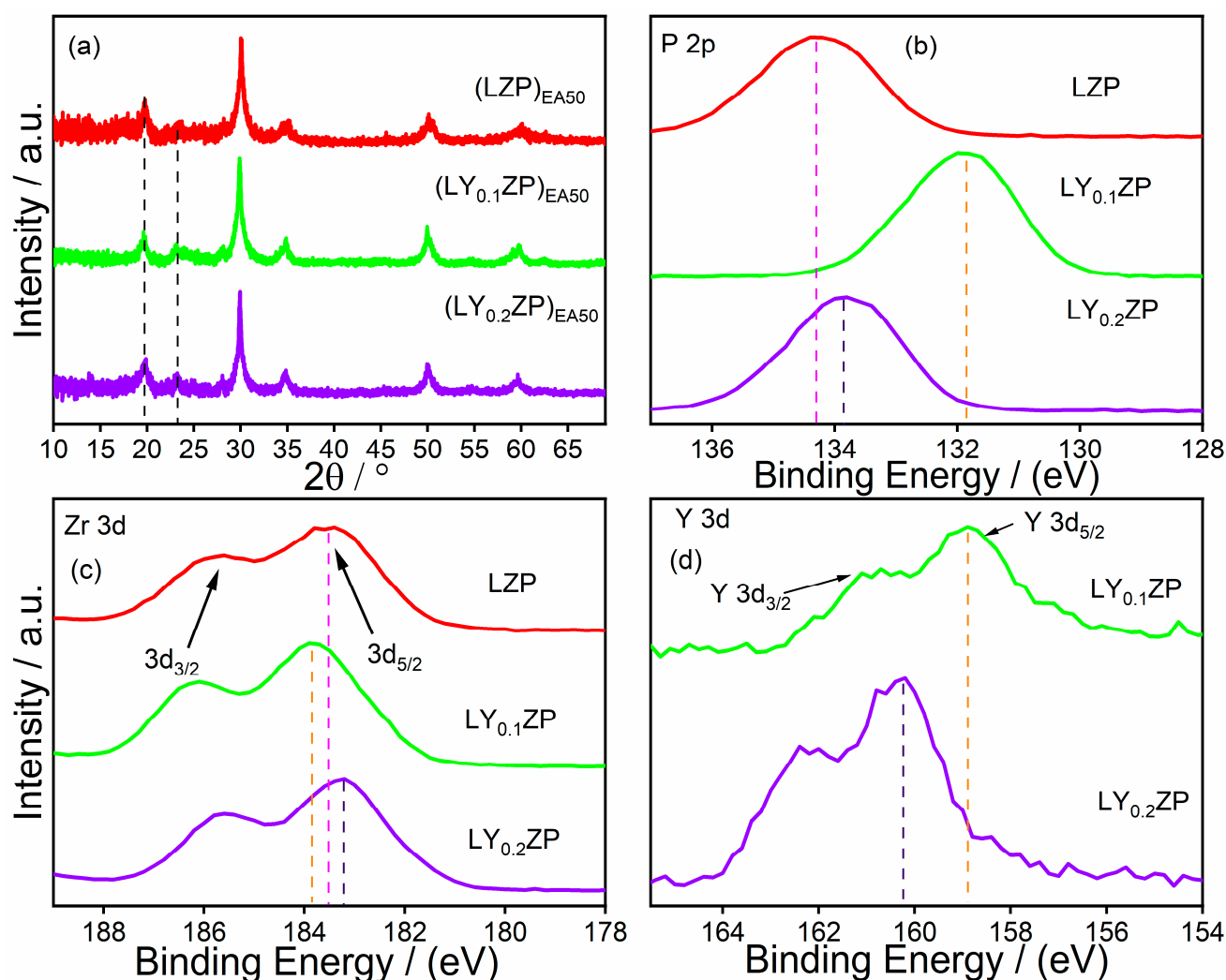


**Figure S4.** (a), (c) XRD patterns comparison before and after annealing at 1150 & 1300 °C of  $(LY_{0.2}ZP)_{PA}$  and  $(LY_{0.2}ZP)_{EA}$  respectively, for 1 h under O<sub>2</sub>. (b), (d) corresponding detailed illustration in the range of 10° to 35°  $2\theta$ ,  $\alpha$  refers to rhombohedral phase  $Li_{1+x}Y_xZr_{2-x}(PO_4)_3$  and  $\beta$  refers to orthorhombic phase  $Li_{1+x}Y_xZr_{2-x}(PO_4)_3$ . (e), (f) phase composition of material from  $(LY_{0.2}ZP)_{PA}$  and  $(LY_{0.2}ZP)_{EA}$  respectively using Rietveld refinement after annealing at 1300 °C for 1 h under O<sub>2</sub>.



**Figure S5.** Raman spectroscopy of materials from  $(LY_{0.2}ZP)_{PA50}$  after sintering at different temperature conditions for 1 h under O<sub>2</sub>. All absorptions bands in dotted rectangular indicates the presence of m-ZrO<sub>2</sub>, while the dotted line is attributed to P-O stretching.

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**Figure S6.** (a) Compositions of as-synthesized materials from experiments involving solvent mixture ethanol/2-EHA (1:1 by volume). Point-point-dash lines refer to new present peaks compared to the compositions of as-synthesized particles from case (LY0.2ZP)<sub>PA50</sub>. XPS results from (b) P 2p. (c) Zr 3d. (d) Y 3d from experiments involving solvent mixture 'B' with varying Y<sup>3+</sup> doping.

**Table S2.** Comparison of as-synthesized average particle size

Nomenclature	As-synthesized average particle size [nm]			
	Specific Surface area [m <sup>2</sup> /g]	BET	TEM	Refinement (m-ZrO <sub>2</sub> )
(LY <sub>0.2</sub> ZP) <sub>PA50</sub>	5.7	180.6	25.7	27.2 ± 0.8
(LY <sub>0.2</sub> ZP) <sub>EA50</sub>	122.1	8.9	7.8	3.6 ± 0.7
(LY <sub>0.1</sub> ZP) <sub>EA50</sub>	129.0	8.4	7.8	14.8 ± 0.4
(LZP) <sub>EA50</sub>	116.7	9.3	9.1	9.6 ± 5.5

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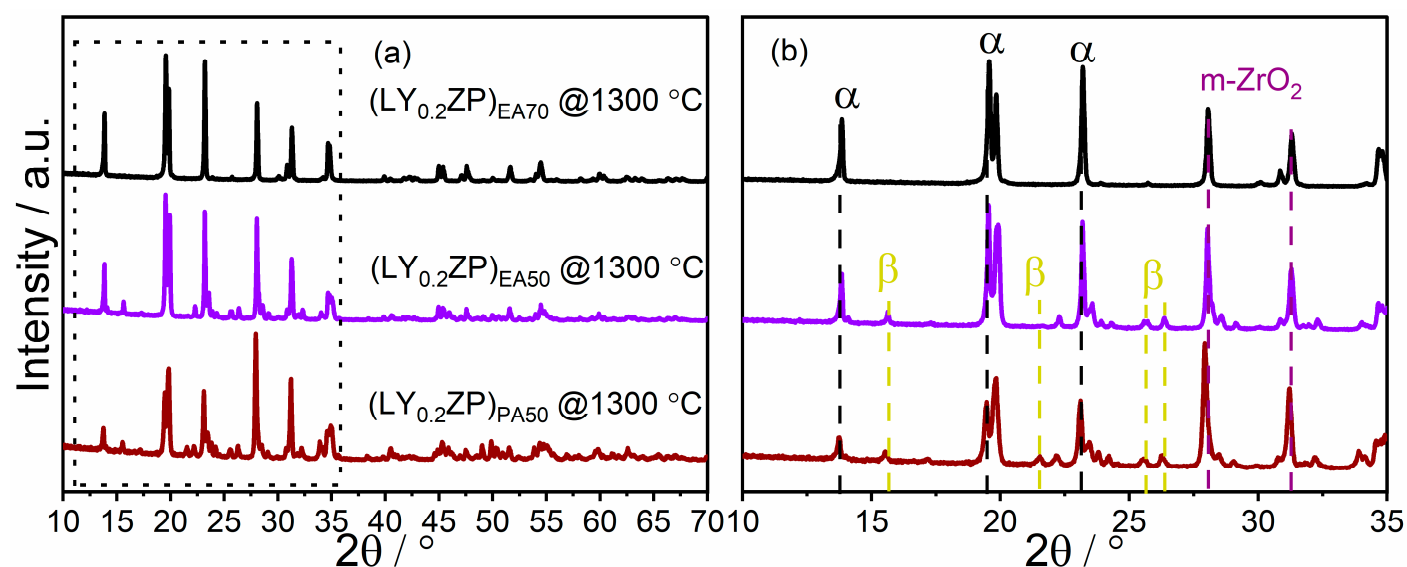
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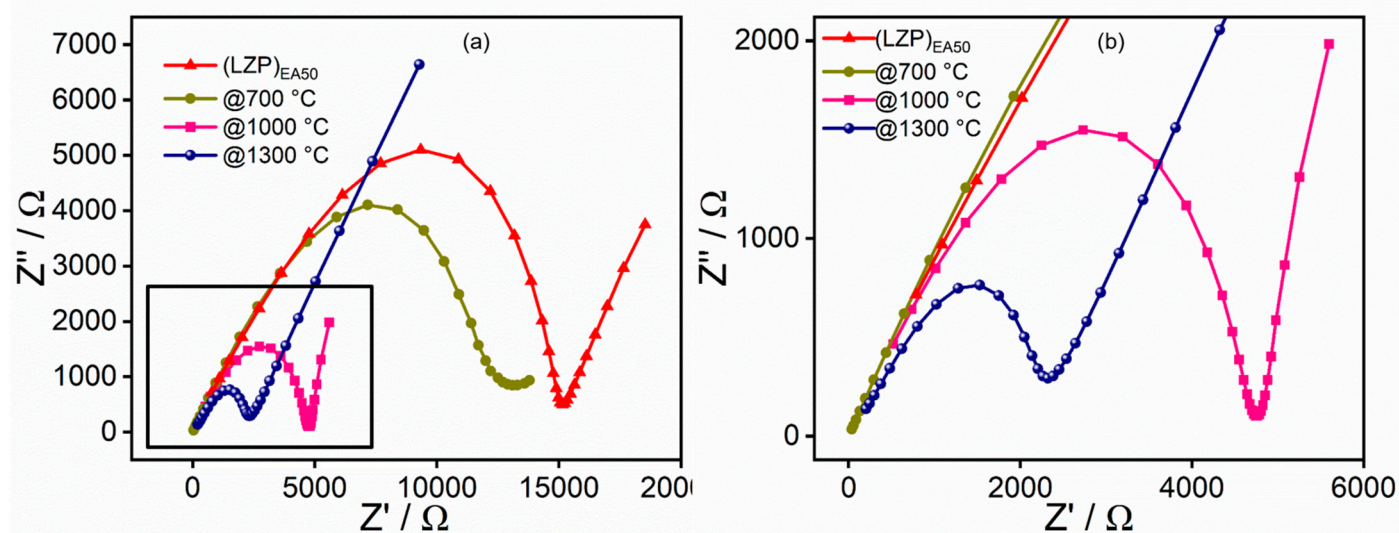
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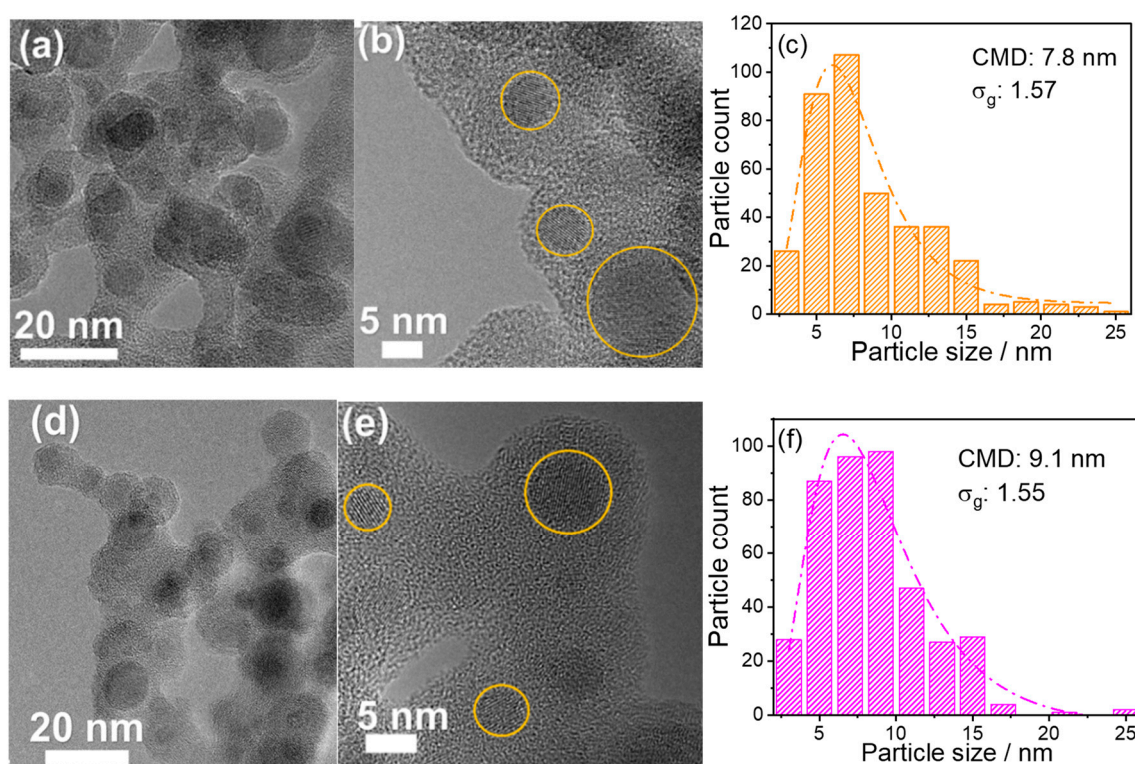


**Figure S7.** (a) XRD patterns of materials from  $(LY_{0.2}ZP)_{PA50}$ ,  $(LY_{0.2}ZP)_{EA50}$  and  $(LY_{0.2}ZP)_{EA70}$  (from bottom to top) after annealing at different temperature conditions for 1h under  $O_2$ . (b) corresponding detailed illustration in the range of 10° to 35°  $2\theta$ .  $\alpha$  and  $\beta$  refers to rhombohedral phase and orthorhombic phase of  $Li_{1+x}Y_xZr_{2-x}(PO_4)_3$  respectively.



**Figure S8.** Impedance spectra of  $(LZP)_{EA50}$  particles after annealing at different temperatures (a). And (b) represents the zoomed image of the square in (a).





**Figure S9.** (a) TEM (b) HRTEM of particles from (LY<sub>0.1</sub>ZP)<sub>EA50</sub> (c) corresponding particle size distribution and fitted lognormal curve. (d) TEM (e) HRTEM of particles from (LZP)<sub>EA50</sub> (f) corresponding particle size distribution and fitted lognormal curve.

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