Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

In-situ formation of Li_3N-rich interface between lithium and argyrodite solid electrolyte enabled by nitrogen doping

Table S1. Crystallographic data of $Li_{6.25}PS_{4.75}N_{0.25}Cl$ obtained from Rietveld refinement. Refined parameters are shown with errors in brackets.

$Li_{6.25}PS_{4.75}N_{0.25}Cl$ crystal structure from X-ray powder diffraction data; (space group *F-43m*); λ_1(Cu-$K_{\alpha1}$) = 1.5406 Å; λ_2(Cu-$K_{\alpha2}$) = 1.5444 Å a = 9.85544(5) Å; 6.08 % Li_2S; 2.3 % LiCl R_{wp} = 2.43 %; R_p = 1.77 %; χ^2 = 3.46						
Atom	**Site**	**a**	**b**	**c**	**Occ.**	**U_{iso}[Å^2]**
Li1	48h	0.3272(5)	0.0030(7)	0.6729(5)	0.52076	0.085(3)
P1	4b	0.00000	0.00000	0.50000	1.00000	0.0205(5)
S1	16e	0.12169(8)	-0.12169(8)	0.62169(8)	0.93743	0.0318(3)
S2	4d	0.25000	0.25000	0.75000	0.83657	0.0197(6)
S3	4a	0.00000	0.00000	1.00000	0.16343	0.0368(6)
N1	16e	0.12169(8)	-0.12169(8)	0.62169(8)	0.06251	0.0318(3)
Cl1	4d	0.25000	0.25000	0.75000	0.16343	0.0197(6)
Cl2	4a	0.00000	0.00000	1.00000	0.83657	0.0368(6)

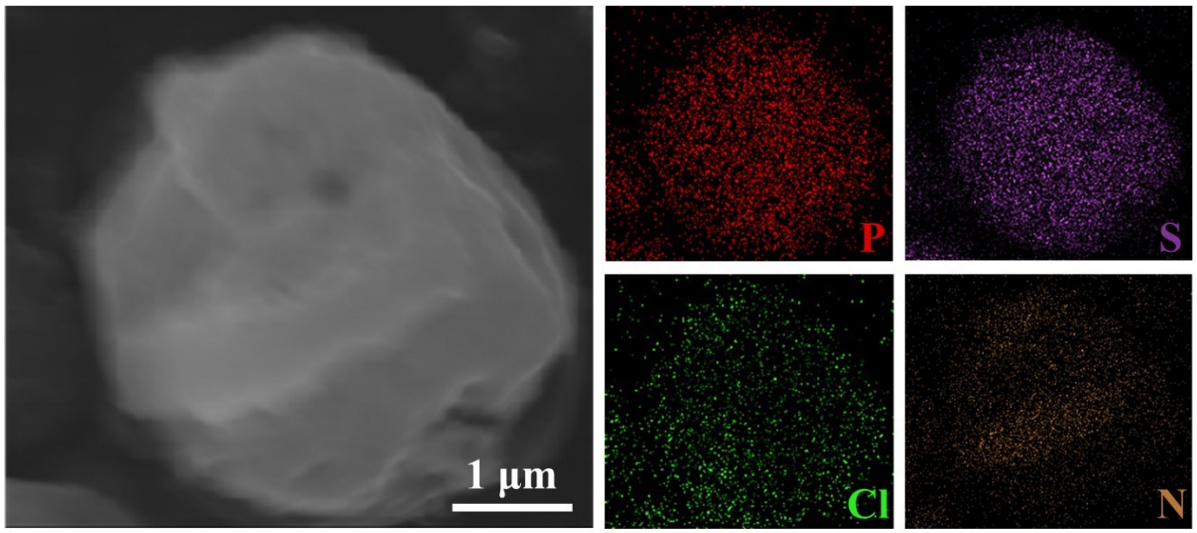

Figure S1. SEM image and EDS mapping of the prepared LPSNC-0.25 sulfide electrolyte powder.

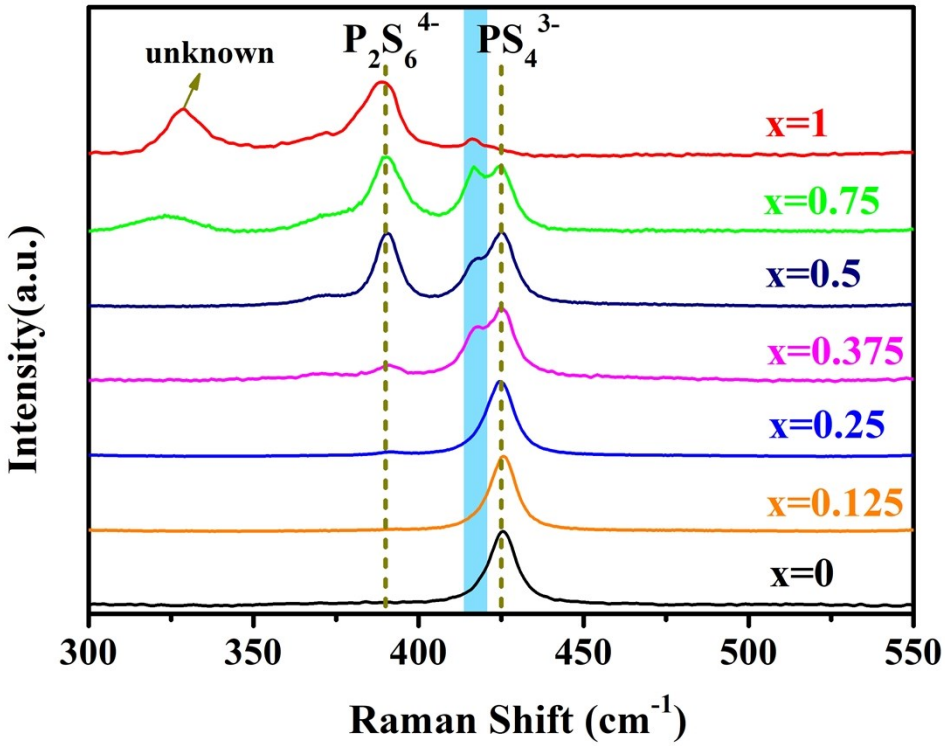

Figure S2. Raman spectra of LPSNC-*x* (*x* = 0–1) electrolyte.

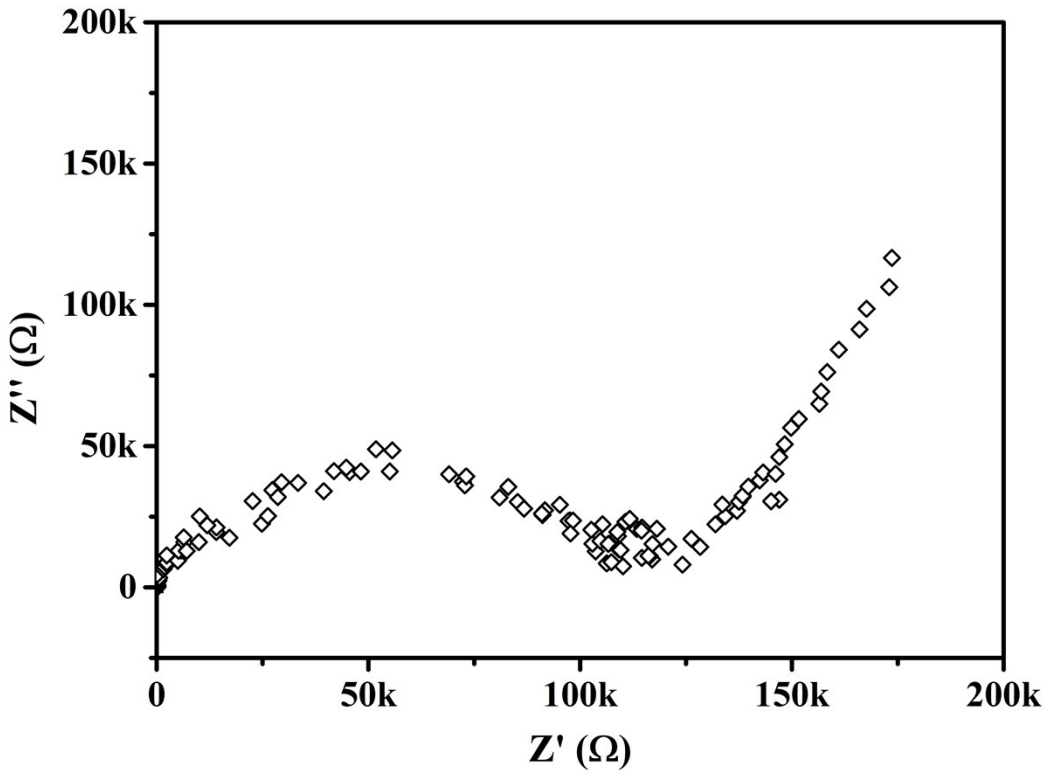

Figure S3. Nyquist plot of the C||LPSNC-1||C blocking cell at room temperature.

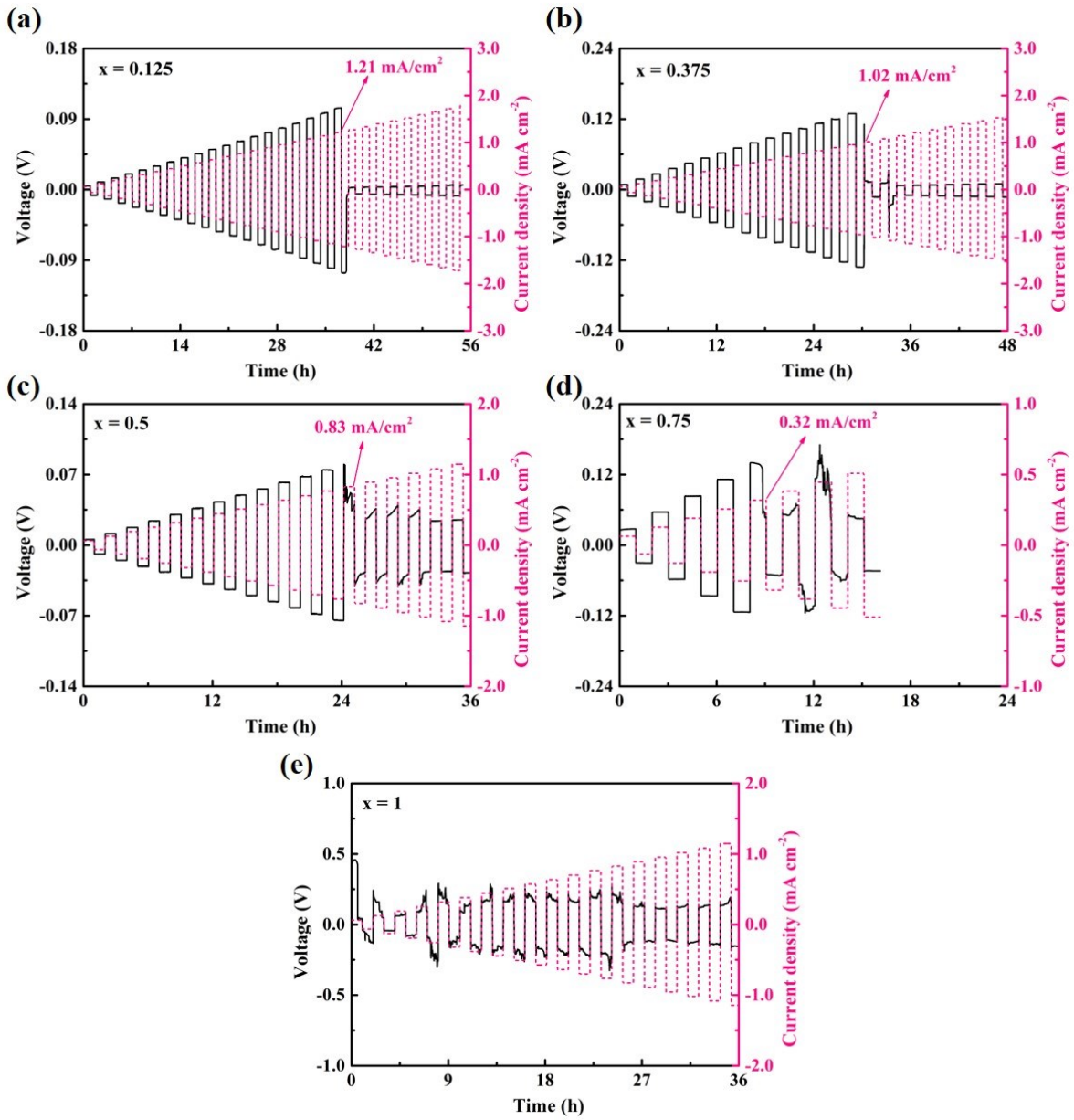

Figure S4. Galvanostatic cycling of Li-Li symmetric cells at step-increased current density at room temperature with $Li_{6+x}PS_{5-x}N_xCl$ electrolytes, where (a) x = 0.125, (b) x= 0.375, (c) x = 0.5, (d) x = 0.75, and (e) x = 1. The time for each plating and stripping is 1 h. The increasing step size of the current density is 0.064 mA cm^{-2}.

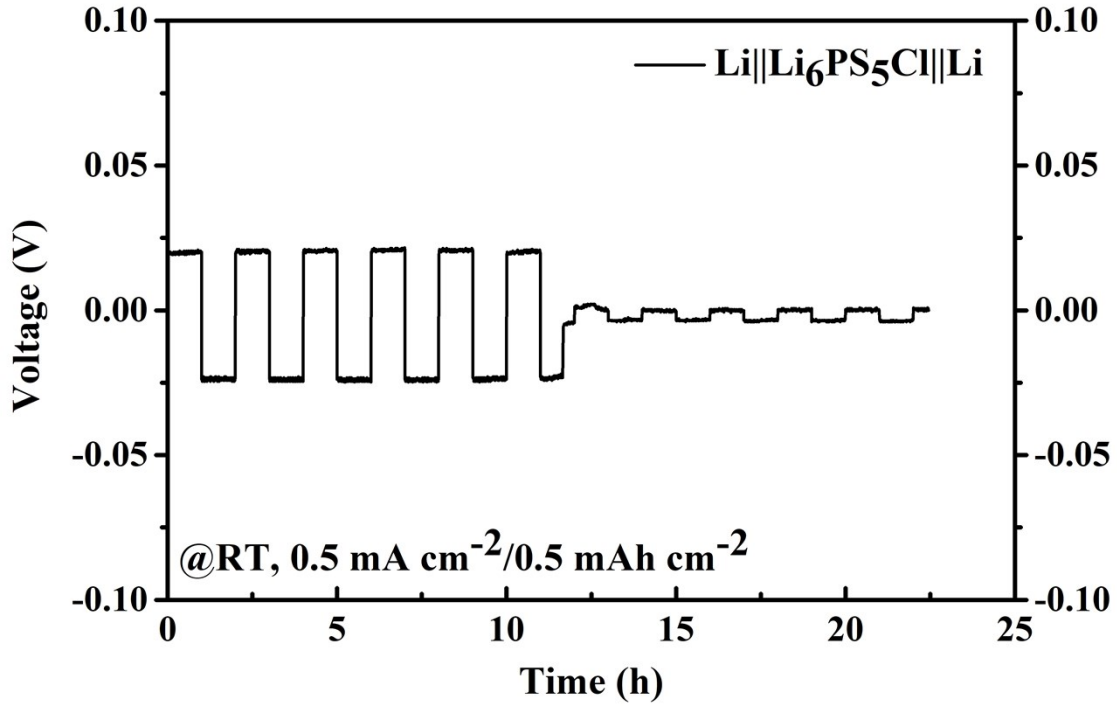

Figure S5. Galvanostatic cycling of the Li||LPSC||Li symmetric cell at the current density of 0.5 mA cm^{-2} and the cut-off capacity of 0.5 mAh cm^{-2} at room temperature.

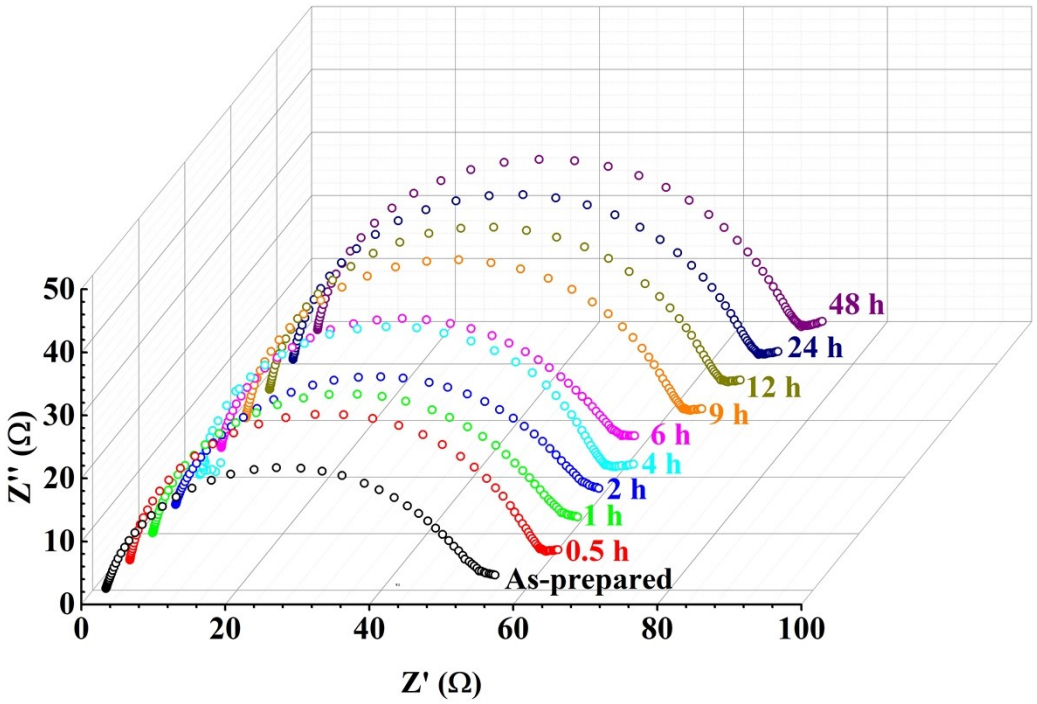

Figure S6. Rest time-resolved EIS plot of Li||LPSNC-0.25||Li.

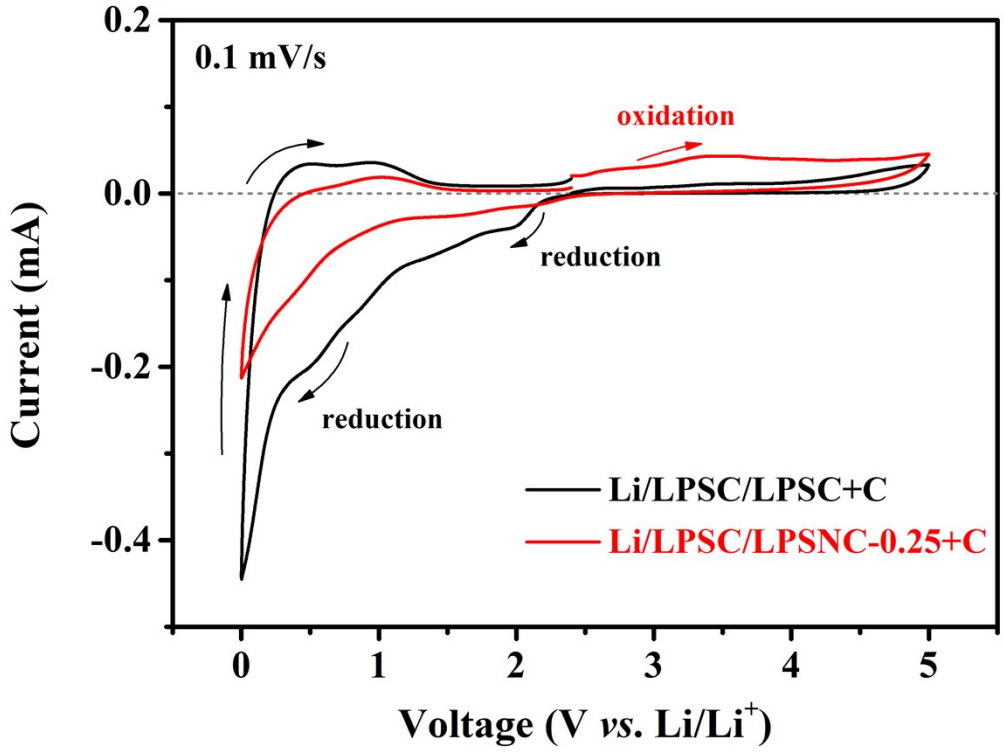

Figure S7. Cyclic voltammetry of Li/LPSC/LPSC+C and Li/LPSC/LPSNC-0.25+C semi-blocking cell at a sweep rate of 0.1 mV/s in the voltage range of 0-5V.

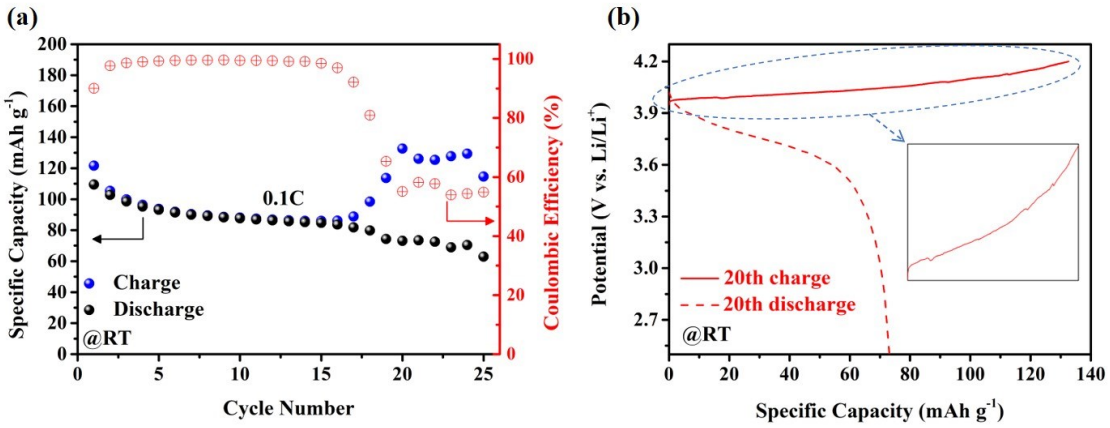

Figure S8. (a) Cycling stability of the Li||LPSC||LCO full cell at room temperature. (b) charge-discharge profile of the 20th cycle of the Li||LPSC||LCO full cell. Inset is the enlarged charging curve with burr, indicating growth of lithium dendrites.

Table S2. Summary of the critical current density and ionic conductivity at room temperature of solid electrolytes.

CCD ($mA\ cm^{-2}$)	Composition	Ionic conductivity (mS/cm)	Reference
>1.26	$Li_{6.2}P_{0.8}Sn_{0.2}S_5I$	0.35	1
1.15	$Li_7La_3Zr_2O_{12}$	0.65	2
0.60	$Li_{6.5}La_{2.9}Sr_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$	0.39	3
0.76	$Li_7P_3S_{11}$	1.55	4
0.88	$Li_7P_{2.9}Si_{0.05}S_{10.85}$	0.80	4
1.05	Li_6PS_5Cl nano-rod	6.11	5
0.55	Li_6PS_5Cl powder	3.50	5
1.16	$Li_7P_{2.88}Nb_{0.12}S_{10.7}O_{0.3}$	3.59	6
0.40	$0.75Li_2S$-$0.25P_2S_5$	0.50	7
1.00	$0.75Li_2S$-$0.25P_2S_5$-0.4LiI	1.40	7
1.50	$0.6Li_2S + 0.32SiS_2 + 0.12PS_{5/2}$	0.10	8
0.90	$Li_6PS_{4.7}O_{0.3}Br$	1.40	9
1.52	$Li_{6.25}PS_{4.75}N_{0.25}Cl$	1.50	This work

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