Supporting Information

2D P-Doped Carbon Nitride as an Effective Artificial Solid Electrolyte Interphase for the Protection of Li Anodes

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		BE	CNP (%At)	CN (%At)
C1s	C-C	284	9.2	7.6
	C-N-P	285.9	12.9	
	C_3-N	286.7		11.8
	C-N pyridinic	288.4	15.2	28.1
	π-π	290.9		
	TOT. %		*37.3*	*47.5*
N1s	N pyridinic	397.4	7.7	24.4
	$C-NH_2$	398.5	10.1	12.5
	C_2-NH	399.7	8.4	11.7
	N-P	400.8	8.4	
	NQ	402.5	2.4	3.9
	TOT. %		*37*	*52.5*
P2p	P-N	133.5	11.5	
	$P-O_3$	135.5	14.2	
	TOT. %		*25.7*	

Table S1. Binding Energy and Chemical composition of CNP and CN powders.

			CNP 1x anode			Non-modified Li anode		
			0s	10s	30s	0s	10s	30s
		BE	%At	%At	%At	%At	%At	%At
C1s	C-Li	282.6	1.7	1.1	1.1	1.2	1	0.9
	C-C	284.4	28.5	11.3	8.8	25	8.5	7.8
	C=O	286.2	6.8	3.3	1.9	5.8	2.1	1.7
	C O$_3$	288.4	3.4	2.1	0.9	2.8	1.7	1.3
	C-SO$_x$	289.4			0.7		0.6	0.6
	C-F	292.5	1.6	0.7	0.5	2.8	0.8	0.6
	TOT. %		*42.1*	*18.5*	*13.9*	*37.6*	*14.7*	*12.9*
N1s	Li3N	398.1	1.8	1.3	0.9	1.4	0.8	0.4
	LiTFSI	400	1.5	1.4	1	1.6	1.4	1
	TOT. %		*3.3*	*2.7*	*1.9*	*3*	*2.2*	*1.4*
O1s	Li2O	528.5	1.2	3.1	4.2	0.8	2.6	3.6
	LiHCO3	531.8	15	14.7	11.3	12.8	13.6	11.8
	C=O	533.1	6.2	1.1	2.2	8.1	2.2	2.1
	TOT. %		*22.4*	*18.9*	*17.7*	*21.7*	*18.3*	*17.5*
F1s	LiF	685.3	3.9	16.9	17.3	12.4	23.4	26
	LiTFSi	688.8	8.4	3.1	2.1	3.8	3.5	2.6
	TOT. %		*12.3*	*20*	*19.4*	*16.2*	*26.9*	*28.6*
P2p	Li-N	133.4		0.2	0.3			
	LiPO$_x$F$_y$	136.1	0.7	0.6	1			
	TOT. %		*0.7*	*0.8*	*1.3*			
S2p	Li$_2$S	160.2	0.6	1	1.1	0.4	0.9	1.4

	Binding Energy (eV)						
	161.9		0.4	0.5		0.5	0.5
Li_2S_x	164		0.3	0.2	0.3	0.4	0.4
SO_3	167.2	2	0.9	0.9	2.4	1.2	1.2
SO_4	168.9	1.8	0.5	0.2	2.5	0.6	0.5
TOT. %		*4.7*	*3*	*2.7*	*5.6*	*3.6*	*4*
Li	*TOT. %*	*14.5*	*36.1*	*43.1*	*15.9*	*34.3*	*35.6*

"**Table 2.** Binding Energy and Chemical composition of CNP modified and non-modified Li electrodes cycled at 3mA/cm^2 for 150 cycles"
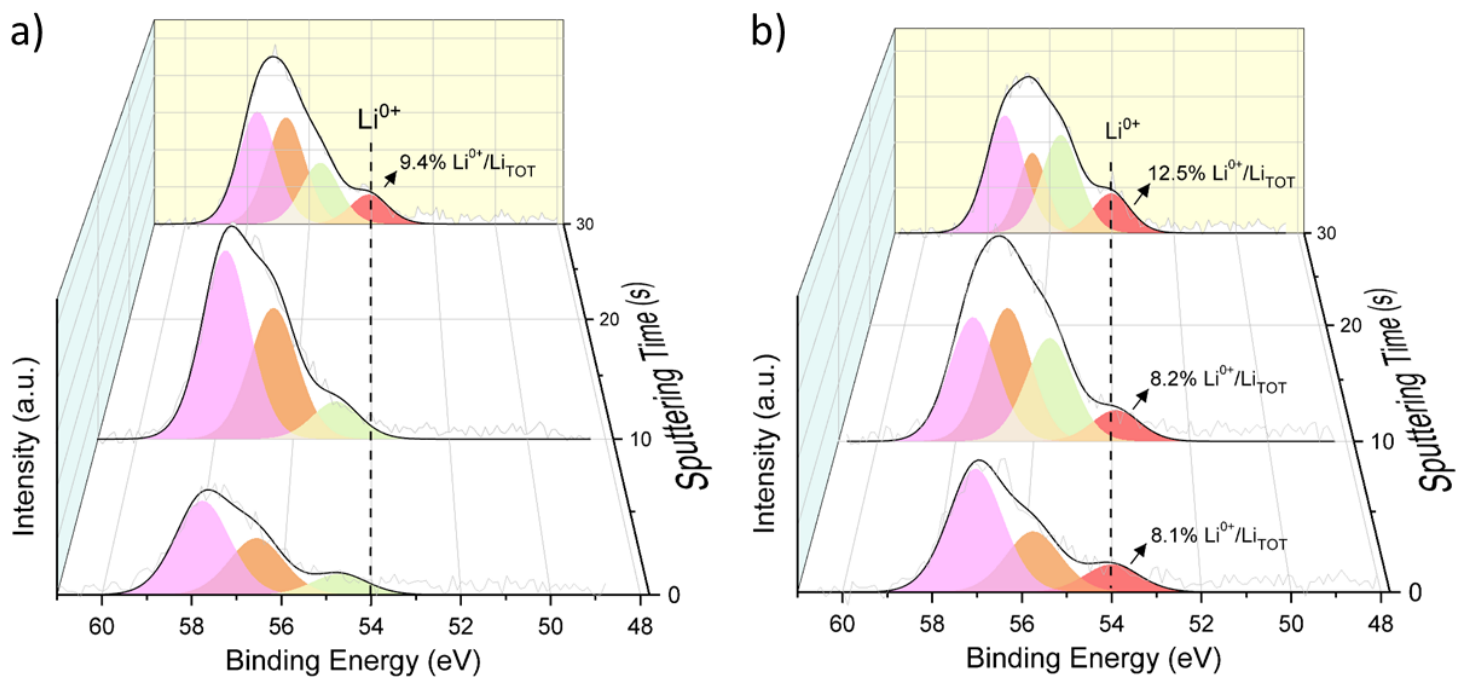
Figure S1. Li 1s detailed spectra for the XPS depth profile of a a) Li and b) CNP1x anode after 150 cycles of Li plating/stripping at current density of 3mA/cm^2 and a cycling capacity of 1mAh/cm^2.

Building the computational model for CNP

Full convergence studies of the calculation parameters were performed on the pristine g-C_3N_4 structure, modeled by a single layer of a 2✕2 slab. In all cases, full geometry optimization of all cartesian coordinates and the cell vectors in the xy-plane (ie. the plane parallel to the surface) was performed. Different doping configurations were evaluated by replacing either a C or a N atom with a P atom. In the first approximation, the different equivalent C o N atoms, as indicated in Fig. S1, were considered as potential doping sites.
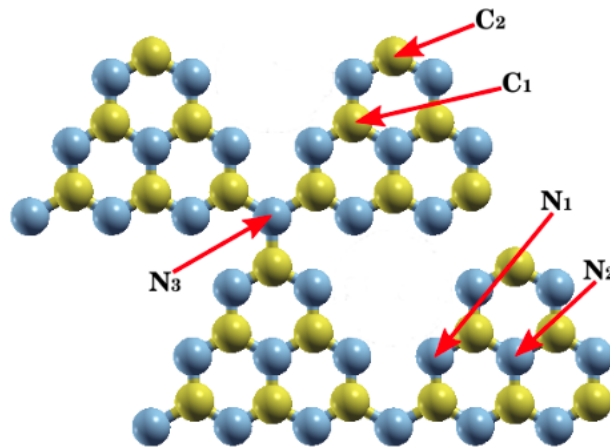
Fig. S2: Different C/N doping positions in pristine g-C_3N_4.

Doping energies were calculated using the following equation:

$$E(\text{doping}) = E(\text{CNP}) - E(\text{CN}) + \Delta H_f(\text{C/N}) - \Delta H_f(\text{P})$$

where E(CN) and E(CNP) are the energies of the fully optimized structures for pristine g-C_3N_4 and the different P-doped materials, respectively, and ΔH_f(C/N/P) are the corresponding elemental enthalpies of formation. These values were taken from the NIST Standard Reference Data

[https://www.nist.gov/srd] and are: $\Delta H_f(C) = 7.43$ eV, $\Delta H_f(N) = 1.98$ eV and $\Delta H_f(P) = 3.28$ eV.

The calculated E(doping) values are summarized in Table S1:

Table S1: Doping energies, E(doping), for the different CNP structures obtained by replacing either a N atom (N-doped) or a C atom (C-doped) in pristine g-C_3N_4.

CNP / N-doped	E(doping), eV		CNP / C-doped	E(doping), eV
N1	-372.27		C1	-502.66
N2	-371.35		C2	-502.29
N3	-372.04			

The absolute values are certainly not comparable to any experimental measure. This is due to the reference adopted for the atomic species, ie. the elemental ΔH_f values. Regardless of this, it is interesting to note that replacing either N_1 or N_3 is energetically more favorable than N_2, and that C-doped structures are relatively more favorable than N-doped ones. Specifically, C_1 is the most likely doping site to produce graphitic P-doped structures. This result is consistent with experimental findings reported in the literature [R. Škuta *et al.* Applied Surface Science 552 (2021) 149490].

Additional P atoms were incorporated into the CN structure by gradually replacing C_1 atoms in the 2✕2 slab. For instance, for the incorporation of the second P atom, starting from the optimized CNP structure that resulted from the replacement of a C1 atom in pristine g-C_3N_4 (labeled as g-CNP_1 in Fig. S2 and corresponding to entry C1 under CNP / C-doped in Table S1), all remaining non-equivalent C_1 positions were evaluated. From all these different structures, the one that yielded the most favorable from an energetic point of view is the one labeled as g-CNP_2 in Fig. S2. Following this protocol, the doping percentage gradually increased yielding the doped

structures shown in Fig. S2. The structure in which 8 C_1 atoms were replaced by P, ie. corresponding to a doping of 14% (g-CNP$_8$ in Fig. S2) is our model for CNP that was employed to study the interaction with lithium, as it is described in the manuscript.
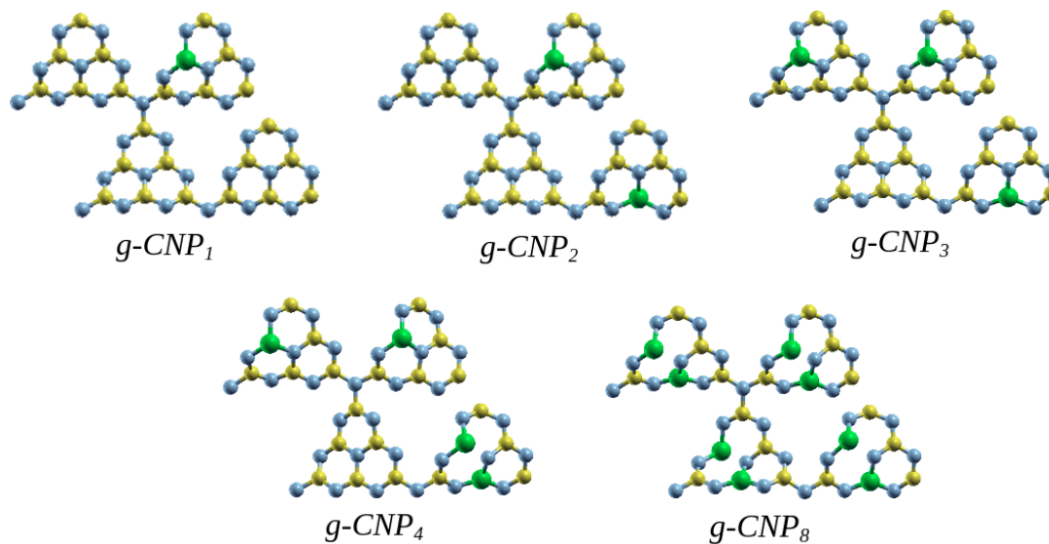

Fig. S3: Most stable structures for different percentages of P-doping pristine g-C$_3$N$_4$ by replacing C_1 atoms.