SUPPLEMENTARY INFORMATION

Single-Walled Carbon Nanotubes as Stabilizing Agents in Red Phosphorus Li-Ion Battery Anodes

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Table S1 – Literature review of red P-C composite based anodes for LIB (mAh/ g_{total} refers to the capacity per mass of the composite; mAh/ g_p refers to the capacity per mass of red P only).

Reference	First discharge	Capacity % loss	Current density	Amount of red P
	capacity	after 50 cycles		in the composite
1	2133 mAh/g _{total}	53 %	130 mA/g _{total}	80 wt%
2	1876 mAh/g _{total}	47 %	100 mA/g _{total}	70 wt%
3	1129 mAh/g _{total}	12 %	205 mA/g _{total}	32 wt%
4	2588 mAh/g _{total}	67 %	100 mA/g _{total}	47 wt%
5	2790 mAh/g _{total}	46 %	150 mA/g _{total} for first 5 cycles, then	47 wt%
			300 mA/g _{total}	
6	2517 mAh/g _p	29 %	130 mA/g _p for 1^{st} cycle, then 300	70 wt%
			mA/g _p	
7	1971 mAh/g _{total}	34 %	140 mA/g _{total}	60 wt%
8	740 mAh/g _{total}	35 %	0.1 C*	12 wt%
9	1402 mAh/g _{total}	39 %	260 mA/g _P	34 wt%
10	1200 mAh/g _{total}	38 %	100 mA/g _{total}	31 wt%
This work	508 mAh/g _{total}	22%	150 mA/g _{total}	60 wt%

*the C-rate was not defined by the authors making it impossible to obtain a universal current density value (*i.e.* in mA/g)

Table S1 summarizes literature review of the lithium ion batteries (LIB) anodes based on red phosphorus and carbon allotrope composites. Capacity % loss after 50 cycles was calculated as per the following formula:

$$\% = \frac{1^{st} Discharge Capacity - 50^{th} Discharge Capacity}{1^{st} Discharge Capacity} x 100$$

As the **Table S1** shows, some authors report the specific gravimetric capacity and/or current densities per mass of P only (mAh/g_p) . We believe that such a value is not entirely correct because all capacity is being attributed to the mass of P, when in reality other electrode components may be contributing factors (the

immediate consequence is the specific gravimetric capacity will appear higher). Secondly, if the C-rate is going to be used as a measure of current density, then it is advisable to define what 1 C equals in mA/g so that the performance can be compared with other reports in the literature. In practice, 1 C should be equal to the theoretical capacity of the complete composite (by including all electrochemically active species in the electrode) that can be discharged in one hour. Referring the C-rate to the mass of P, when P is not the only electrochemically active species, will make the current density appear higher because for phosphorus 1 C = 2596 mA/g.

While the **Table S1** lists only a small number of red P-C reports (these were all we could identify from the literature), the loading of P in the composites is seen to vary widely, from 12 to 80 wt%. Naturally, this makes it more complicated to compare the performance of the composites in particular when accessing the stability over tens of cycles. Still, for those with P loadings closer to our case (high loadings of >50%), the stability achieved by us is clearly superior.



Figure S1 – a) Pulverization and loss of electrical contact between red P particles during charging/discharging; b) Electrical contact loss between red P particles is prevented due to SWCNT stabilization role.



Figure S2 - XPS spectra for a P-SWCNT 7:3 composite: a) survey spectrum, b) O1s level spectrum, c) C1s level spectrum.

Fig. S2a shows the presence of P, C and O. The O 1*s* spectrum (**Fig. S2b**) can be deconvoluted into three different peaks, one at 531.5 eV that can be attributed to the double bonded oxygen with carbon and phosphorus (C=O and P=O), one at 532.9 eV attributed to the single bonded oxygen in C-O and one at 533.1 eV that corresponds to the symmetric oxygen bridging in P-O-P.^{11, 12} In **Fig. S2c** three different peaks can be identified for the C 1*s* spectrum. The peak positioned at 284.1 eV is attributed to the C-C bond, the one at 285.3 eV to the C-O bond and the one at 289.3 eV is attributed to the O-C=O bond.^{11, 13}



Figure S3 – a) Moisture captured by the hygroscopic phosphorus oxide surface after 15 min in ambient conditions; b) FTIR of the electrode surface before and after removal of the surface moisture (droplets were removed by absorbing them with a tissue).



Figure S4 – SEM micrographs of a) red P particles and b) SWCNT; TEM micrographs of c) red P and d) SWCNT; e) Low and f) high magnification SEM micrographs of the composite.

The starting amorphous red P (**Fig. S4a**) was firstly ground and then characterized by SEM, whereby it was seen that the size of the majority of the particles was in the single digit micron range. Active materials with larger particle size are favorable in practical applications to achieve higher energy density.¹⁴ This confirms that manual grinding for 60 min using pestle and mortar is an effective way of reducing the particle size, in addition to breaking the branch-like structure of the starting red P. The SEM micrograph of SWCNT (**Fig. S4b**) shows a disordered network of nanotubes that are closely interconnected, with small-sized empty spaces in between the bundles that can be filled with phosphorus. Having a composite with such closely intertwined filler and matrix is believed to provide a mechanically stable material that can withstand stresses during the lithiation and delithiation of P. **Figs. S4c** and **S4d** are TEM images of the red P and SWCNT, respectively. **Figs. S4e** and **S4f** show the low and high magnification SEM micrographs of the composite, respectively, and confirm its heterogeneous nature.



Figure S5 – a) TEM micrograph of SWCNT catalyst particles covered with a graphitic shell and b) corresponding EDX spectrum of SWCNT (*indicates contamination from the glass microfiber substrate on which the TEM grid was placed before transfer into the TEM).



Figure S6 – Differential capacity plot (dQ/dV) of the composite's 10th cycle at 150 mA/g showing three lithiation/alloying and delithiation/dealloying peaks (indicated by the * symbol).



Figure S7 – SEM images of the composite electrode a) before and b) after 70 charge/discharge cycles at 300 mA/g.

Whereas the electrode's surface before the electrochemical measurements (**Fig. S7a**) is smooth and crackfree, it becomes rougher and sectioned after 70 charge/discharge cycles (**Fig. S7b**). This behaviour is expected and is due to the repeated red P volumetric changes during cycling of the cell. Still, the composite electrode remains firmly in contact with the current collector. As explained in the main text this is attributed to the synergetic effect between red P and SWCNT.



Figure S8 – Charge/discharge voltage profiles at a current density of 150 mA/g for the source materials, a) red P and b) SWCNT; Cycling stability at a current density of 150 mA/g for c) red P and d) SWCNT.



Figure S9 – Cycling stability of red P at a current density of 50 mA/g.



Figure S10 – Nyquist plot of the red phosphorus and composite electrodes. The inset shows the equivalent circuit used to fit the data.

The experimental EIS spectra, for both the red P and the composite, have been fitted with the equivalent circuit show in **Fig. S10** inset.^{15, 16} The elements of the equivalent circuit are as follows: internal resistance of the electrochemical cell and the electrolyte (R_i), the SEI layer resistance (R_s), charge transfer resistance (R_{ct}), Warbug impedance (W), a constant phase element (CPE-1) and a non-ideal constant phase element (CPE-2).



Figure S11 – Optical images of: a) the red P electrode after 50 charge/discharge cycles at 50 mA/g, where the dark patches correspond to the preserved active material coating; b) the composite electrode after 100 charge/discharge cycles at 750 mA/g.

From **Fig. S11**, it is clear that despite the composite electrode being cycled for a larger number of cycles at higher current density, its integrity is preserved when compared to the red P-only electrode. This attests well the stabilizing effect of the SWCNT additive.

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