## **Electronic Supplementary Information (ESI)**

## Steady cycling of lithium metal anode enabled by alloying Sn-modified carbon nanofibers

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**Fig. S1** The top-view and cross-sectional SEM images of (a and b) Sn/CNF and (c and d) CNF films.



Fig. S2 (a)  $N_2$  adsorption isotherms of Sn/CNF and CNF films and (b) the corresponding pore size distribution curves.



Fig. S3 TGA curves of Sn/CNF and CNF films under air atmosphere at 10 °C min<sup>-1</sup>.

During TGA testing, Sn is oxidized to  $SnO_2$  under air atmosphere after annealing above 220 °C.<sup>1,2</sup> The calculated Sn content is based on the following Equation S1:

$$\operatorname{Sn} + \operatorname{O}_2 \longrightarrow \operatorname{SnO}_2$$
 (S1)

The mass increase of Sn transformed into  $SnO_2$  is 27%. We supposed the mass percentage of Sn in the Sn/CNF is m, so the remainder mass percentage attributed to the weight decrease is (1–m). According to the computational formula:

1 - m - 27% m = 60%

Then, we can get m = 32%.



Fig. S4 The magnified view of voltage–capacity profile of Sn/CNF at 0.5 mA cm<sup>-2</sup> for Sn/CNF.



Fig. S5 Cyclic voltammetry scan of (a) Cu, (b) CNF and (c) Sn/CNF with a counter electrode of Li metal at a scan rate of 0.05 mV s<sup>-1</sup>.



**Fig. S6** The Nyquist plots of Sn/CNF||Li, CNF||Li and Cu||Li cells after plating of 10 mAh cm<sup>-2</sup> Li.



Fig. S7 Coulombic efficiency for Li deposition/stripping in Sn/CNFIILi half cells at the current density of 1 mA cm<sup>-2</sup> with the capacity of (a) 2 mAh cm<sup>-2</sup> and (b) 3 mAh cm<sup>-2</sup>.



Fig. S8 The simplified equivalent circuit for fitting the impedance spectra of EIS plots.

**Table S1.** The fitted electrochemical resistance values of Sn/CNF@Li, CNF@Li andCu@Li electrodes for symmetrical cells.

Sample	State	$R_{s}\left(\Omega ight)$	$\mathrm{R}_{i}\left(\Omega ight)$	$R_{ct}\left(\Omega ight)$
Sn/CNF@Li	Fresh	5.9	12.7	4.1
	10th cycle	4.3	4.3	1.8
CNF@Li	Fresh	4.6	33.8	27.0
	10th cycle	5.2	11.1	2.6
Cu@Li	Fresh	4.6	46.5	48.0
	10th cycle	7.3	11.2	6.4



**Fig. S9** SEM images of Cu foil at different Li plating/stripping states for (a) plating 10 mAh cm<sup>-2</sup>, (b) stripping 5 mAh cm<sup>-2</sup>, (c) stripping 10 mAh cm<sup>-2</sup>, (d) further plating 5 mAh cm<sup>-2</sup> and (e) plating 10 mAh cm<sup>-2</sup>.



**Fig. S10** SEM images of of (a–c) Sn/CNF@Li and (d–f) CNF@Li electrodes after 50 cycles at 1 mA cm<sup>-2</sup> with a fixed capacity of 1 mAh cm<sup>-2</sup> for symmetrical cells.



**Fig. S11** Typical charge–discharge profiles of (a) Sn/CNF@Li||LFP, (b) CNF@Li||LFP and (c) Cu@Li||LFP at 0.5 C.



**Fig. S12** (a) Cycling performance of Sn/CNF@Li||LFP cell at 1 C with LFP cathode loading of 10 mg cm<sup>-2</sup>. (b) Area capacity comparison and (c) the voltage–area capacity profiles of the cells with different loadings of LFP.

## References

- S1 N. Zhang, Q. Zhao, X. Han, J. Yang and J. Chen, *Nanoscale*, 2014, **6**, 2827-2832.
- S2 H. Zhang, X. Huang, O. Noonan, L. Zhou, C. Yu, Adv. Funct. Mater., 2017, 27, 1606023.