# **Supplementary information**

# Uniform distribution of metallic lithium and carbon in nanoscale for

## highly stable carbon-based lithium metal anode

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#### **I. Supporting Text**

#### **1. Experimental Section**

#### 1.1. Electrode material preparation and cell assembly methods

The composite lithium metal anode (LMA) was prepared using stabilized lithium metal powder (SLMP, China Energy Lithium Co., Ltd.) and carbon nano-powders (commercial Ketjenblack®EC-300J, KB, Lion Specialty Chemicals Co., Ltd. or graphitized KB at 2800 °C, GKB) by ball milling, labeled as KBLi or GKBLi. Briefly, the mixture of SLMP and carbon nano-powders was shaken by ball milling at 200 rpm for 12 h with Ar atmosphere. Then rolled in a roller press (Specac Co., Ltd., P/N GS03950) into circular disks ( $\Phi$ 8 mm) as an anode in the dry air room (constant temperature 25°C, relative humidity 20%). We found that too much amount of carbon powder is difficult to form fixed shape electrode, and too less will also cause a large amount of lithium to stick. When the molar ratio of carbon powder and lithium powder is 1:7, the composite powder is easily pressed into self-supporting electrode. Therefore, this ratio was used in all this article, and the total amount of raw materials for ball milling was 1g each time. The LiFePO4 (LFP) electrodes were purchased from Nanjing Mojisi Energy Technology Co. Ltd. The mass loading of active LFP was ~4 mg/cm<sup>2</sup>.

Assembly of symmetric cells. The symmetric cell of 2032-type coin cell were assembled by two same prepared electrodes as anode and cathode in an argon-filled glove box. Polypropylene (Celgard 2500) was used separator, and 1 M lithium bis(trifluoromethane)sulfonamide (LiTFSI) dissolved in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (at a volume ratio of 1:1) with 2 wt% LiNO<sub>3</sub> as an electrolyte.

Assembly of full cells. In full cell tests, the prepared electrodes were used as anode and matched with LFP cathode. carbonate-based electrolyte (1 M LiPF<sub>6</sub> EC/DMC with 5 wt% FEC) was used. All the full cells worked in the voltage range from 2.0 V to 4.0 V at 28 °C. The initial 5 cycles of all full cells were performed at 0.1 C rate for activation and then the specified current rate was carried out for cycling tests.

#### **1.2 Material Characterization**

The spectroscopic measurements were obtained using a ZEISS SUPRA 55 SEM at 10 kV and a Hitachi 7700 TEM at 100 kV and a Talos F200X G2 HRTEM at 200 kV. XRD pattern was

collected on a Philips Rigaku D/max 2500B2+/PCX X-ray diffractometer with filtered Cu Ka radiation ( $\lambda$ =1.54056 Å). XPS analysis was carried out on a Thermo Scientific K-Alpha (Al Ka 1486.6eV). Soft X-ray Spectroscopy, specifically X-ray absorption near edge structure (XANES) studies have been performed at the 4B9B photoelectron spectroscopy station, the Beijing Synchrotron Radiation Facility (Institute of High Energy Physics, Chinese Academy of Sciences). XANES were recorded at both C K-edge (from 280 to 320 eV with an energy resolution of 0.2 eV), and N K-edge (from 390 to 420 eV with an energy resolution of 0.2 eV) in total electron yield by using a channeltron. All the spectra were normalized far above the K-edge absorption edge. The sample has been oriented at 55 degrees to the incident X-ray for all the XANES measurement.

#### **1.3 Electrochemical Measurements**

All the galvanostatic overpotential pre-cycle and long-term cycle test of the battery were conducted on a LAND CT3001A battery test system (Wuhan LAND Electronic Co. Ltd., China). Cyclic voltammetry (CV) was tested on an electrochemical workstation (Ahner Zennium) at the different scan rate within a certain voltage range. A dynamic capacitance measurement (DCM) test was conducted by overlying the single-frequency AC current on a DC charging current at 1 mA cm<sup>-2</sup> and 15.0 Hz on Ahner Zennium electrochemical workstation.

### **II. Supporting Figure**



**Figure S1**. SEM images of (a) KB, (c) GKB, (b) spherical SLMP particles (inset for the histograms of diameter distribution) and (d) single spherical SLMP particle.



Figure S2. XRD patterns of GKBLi and the standard cards.



**Figure S3.** XPS survey spectra of (a) SLMP, KBLi and GKBLi; (c) GKB. Highresolution XPS spectra of the (b) N 1s peak of KBLi and GKBLi; the (d) C 1s peak of GKB.



**Figure S4.** Deconvolution of C 1s K-edge XANES spectra of KB, GKB, KBLi and GKBLi.



**Figure S5.** Cycling performances of the Li foil||LFP, KBLi||LFP and GKBLi||LFP full cells at charging/discharging rates of 0.5 C ( $1C = 170 \text{ mA h g}^{-1}$ ).



Figure S6. Charge/discharge cycling performance of Li||LFP cells at 0.5 C.



Figure S7. Rate capacity of Li foil@LFP and GKBLi@LFP cells.



**Figure S8.** The Nyquist plots of Li foil||LFP, KBLi||LFP and GKBLi||LFP cells before cycles (open-circuit voltage).



**Figure S9.** CV curves of full batteries using (a) GKBLi anode, (b) KBLi anode and (c) lithium foil anode under 2.0-4.5 V and 0.2 mV s<sup>-1</sup> of 3 cycles.

The Randles-Sevcik equation (ByungDae Son et al 2020 J. Electrochem. Soc. 167 100549) is given by

$$i_p = (2.69 \times 10^5) n^{3/2} ACD^{1/2} \gamma^{1/2}$$

where  $i_p$  is the peak current, A is the electroactive surface area of the electrode, D is the diffusion coefficient of lithium ions, C is the concentration of lithium ions, g is the scan rate, and n is the number of electrons transferred in the corresponding reaction. The series of D value for each peak of the GKBLi anode cell are shown in Table S1 and are higher than that of the lithium foil anode cell, with increments of 18 and 14%, respectively.



**Figure S10.** The cycle performance of full cells (a) at 0.5 C with lithium carbon composite anode matching NCM811 cathode, the cycle capacity-voltage curve of (b) Li||NCM, (c) GKBLi||NCM and (d) KBLi||NCM full cells.

### **III. Supporting tables**

	GKBLi (cm <sup>2</sup> s <sup>-1</sup> )	KBLi (cm <sup>2</sup> s <sup>-1</sup> )	Li (cm <sup>2</sup> s <sup>-1</sup> )	Increment (%)
D <sub>a</sub>	8.27×10 <sup>-8</sup>	6.10×10 <sup>-8</sup>	7.01×10 <sup>-8</sup>	18
D <sub>c</sub>	5.75×10 <sup>-8</sup>	$3.71 \times 10^{-8}$	5.03×10 <sup>-8</sup>	14

 Table S1. Lithium-ion diffusion coefficient values of reduction peaks (c) and oxidation peak (a).

 Table S2. The summary of the electrochemical cycling performance of carbon 

 lithium metal anodes in the full cells.

Host kinds	Preparation	Ave CE	Current density	Cycles life	capacity retention	Ref.
	method	%		n	%	
C-Li powder	Ball-millng	99.9	2 C	1000	90.9	This
composite			(1C = 170 mA g <sup>-</sup>			work
			1)			
EG-Li powder	Pressing	-	1 C	500	93.5	1
composite	Heating		$(1C = 140 \text{ mA g}^{-1})$			
3D Carbon host	Heating	98.5	2 C	500	~90.1	2
Ionic liquid-	Cryo-milling	99.9	0.2 C	350	92.7	3
protected Li			$(1C = 205 \text{ mA g}^{-1})$			
CNTs-Li	Ball-milling	-	1 C	1100	~91.5	4
composite	Heating		$(1C = 170 \text{ mA g}^{-1})$			
CNTs-Li powder	Mixing	-	0.5 mA cm <sup>-2</sup>	100	~99	5
compsite						
Quicksand-like Li	Heat stirring	-	1 C	400	$\sim 120 \text{ mA h g}^{-1}$	6
Carbon cloth host	Doping Heating	-	1 C	250	90.8	7
Li@C-Ag/PVDF	Electrospinning	98	0.5 C	200	$\sim 148 \text{ mA h g}^{-1}$	8
			$(1C = 170 \text{ mA g}^{-1})$			
Carbon cloth host	Doping	98	1 C	500	75	9
Carbon fiber host	Rolling	-	1 C	140	$\sim 120 \text{ mA h g}^{-1}$	10
			$(1C = 170 \text{ mA g}^{-1})$			

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