Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic supplementary information for

Towards practical cells: Combined use of titanium black as cathode additive and sparingly solvating electrolyte for high-energy-density lithium–sulfur batteries

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Table S1 Target of low-cost practical Li–S batteries with high energy densities (> 500 Wh kg^{-1}).[1]

Parameter	Target
Sulfur content (based on the whole cathode)	≥ 70 wt%
Sulfur loading	> 4 mg cm^{-2}
Specific capacity	≥ 1400 mAh g^{-1}
Cathode porosity	≤ 40%
E/S ratio	≤ 3 μL mg^{-1}
% Li excess	≤ 50 wt%
Preparation and fabrication method (including the material and cathode)	Feasible and low cost

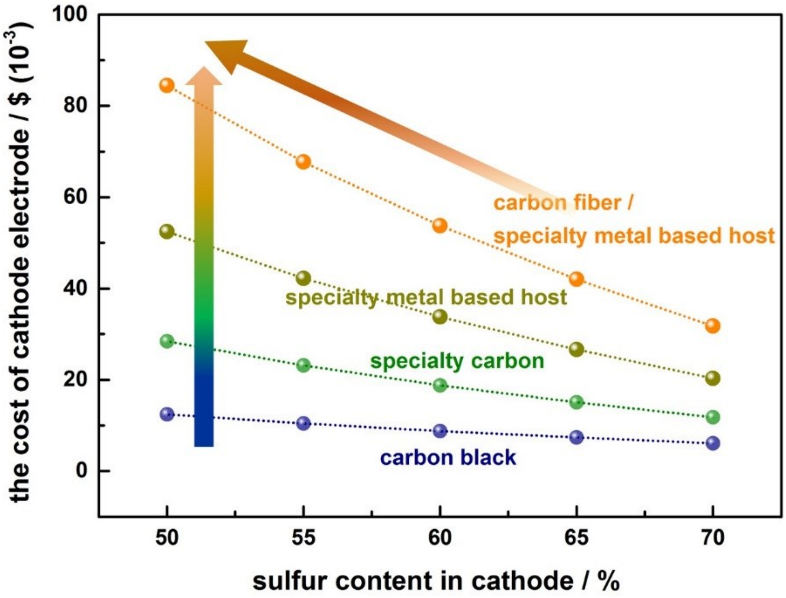

Fig. S1 Cost of sulfur cathode based on a 2 Ah pouch cell with various kinds of carbon material. The lowest cost cathode is based on carbon black, and the highest is with the carbon fiber materials.[6]

Table S2 Comparison of the electrochemical performance of Li-S batteries with Ti-based host materials.

Materials	**Sulfur loading** (mg cm^{-2})	**E/S** (μL mg^{-1})	**Ti content in electrode** (wt%)	**Sulfur content in electrode** (wt%)	**Electrochemical performance** (mAh g^{-1})	**Reference**
TiO/S/C	4.0	—	13-15	56%	821 (50 cycles at 0.05 C)	[2]
Ti_4O_7/S	0.75–0.9	—	—	60–70%	800 (250 cycles at 0.5 C)	[3]
Mesoporous TiN	1.0	—	35	50%	644 (500 cycles at 0.5 C)	[4]
TiO/S/carbon hollow fibre	5	—	—	58%	680 (400 cycles at 0.2 C)	[5]
TiB/S/KB	4.5 (pouch cell)	3.2	5	70–71%	1300 (1st cycle at 1/48 C)	This work
	4.5 (coin cell)	6–7	5	70–71%	650 (200 cycles at 0.1 C)	

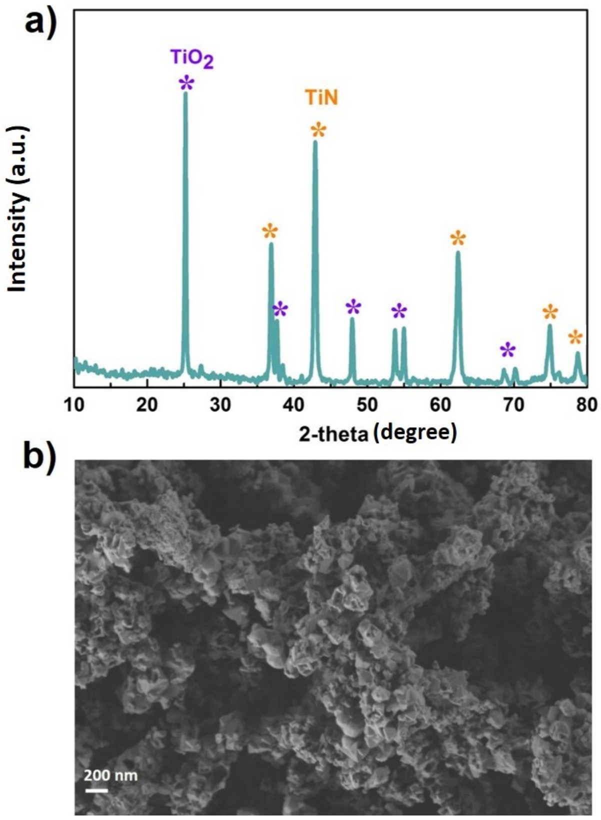

Fig. S2 a) XRD pattern and b) SEM image of the TiB material. The peaks at 36.9°, 43.1°, 62.5°, 74.9°, and 78.7° can be assigned to the (111), (200), (220), (311), and (222) reflections of crystalline TiN, respectively.[7] The other peaks at 25.3°, 37.7°, 48.0°, 55.0°, and 70.0° are ascribed to the reflections from the (101), (004), (200), (105), and (211) planes of TiO_2, respectively.[8]

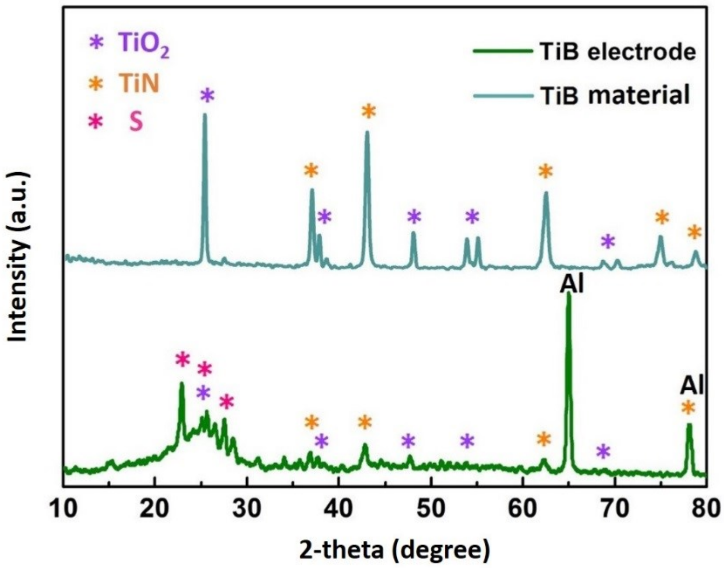

Fig. S3 XRD patterns of the TiB material and TiB electrode.

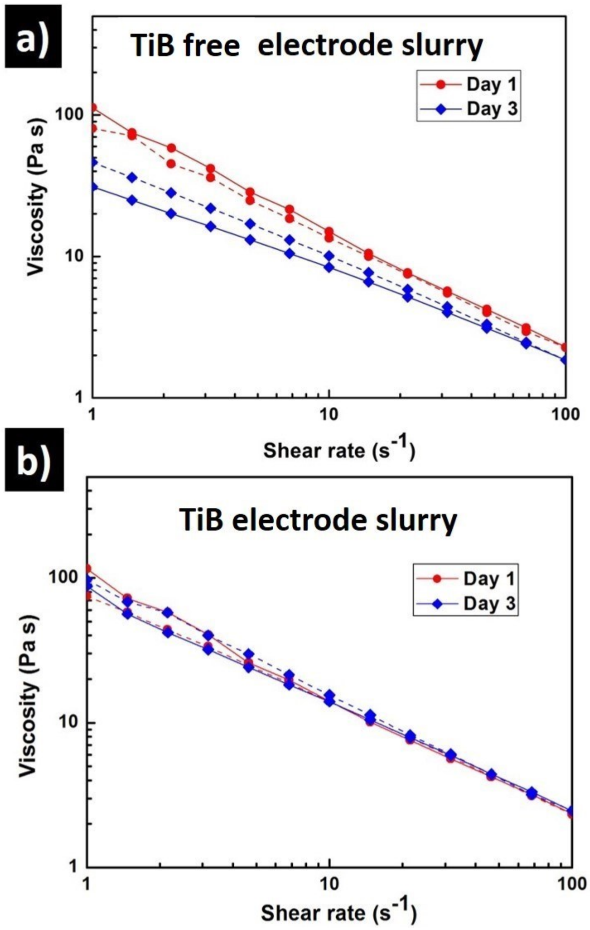

Fig. S4 Variation in viscosity with shear rate of the a) TiB free electrode slurry and b) TiB electrode slurry on the first day (Day 1) and third day (Day 3) after preparationTiB free. Solid and broken lines correspond to measurements taken with increasing and decreasing shear rate, respectively.

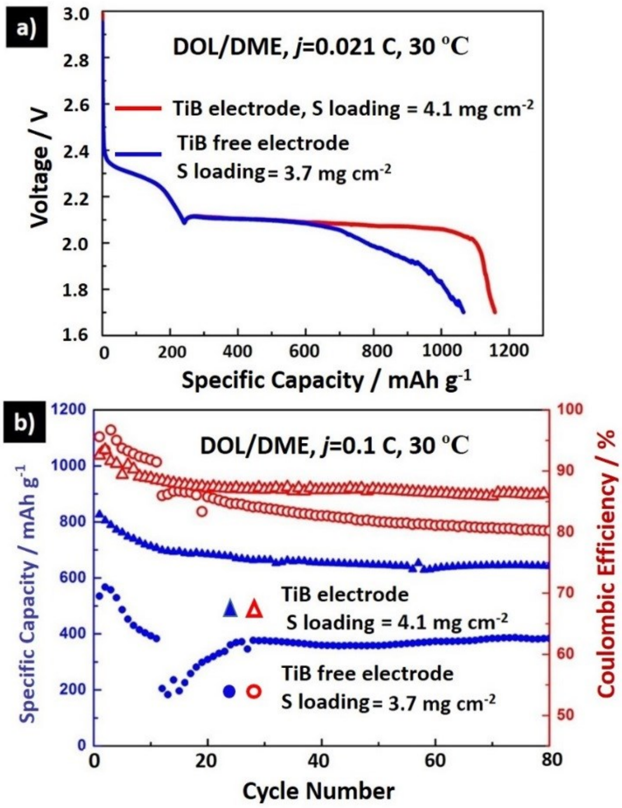

Fig. S5 a) Initial discharge curves of the TiB and TiB free electrodes at 0.021 C and b) subsequent cycling performance and Coulombic efficiency at 0.1 C with 1 M Li[TFSA] in DOL/DME containing 0.5 wt% $LiNO_3$ at E/S = 10 μL mg^{-1}.

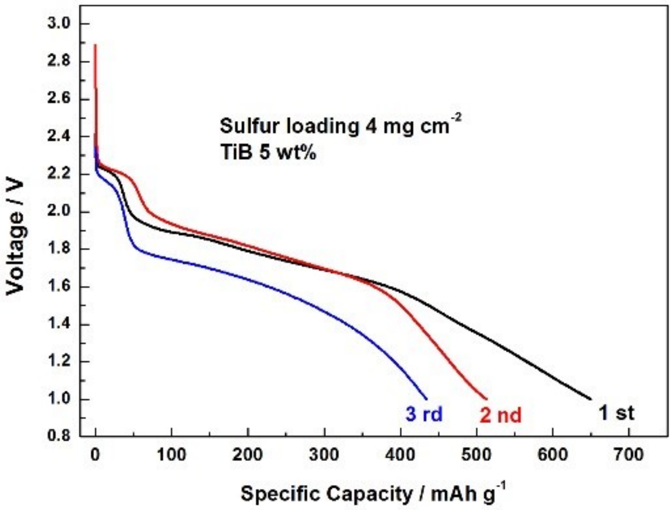

Fig. S6 Initial three discharge curves of TiB electrode (TiB content 5 wt%) at 0.1 C

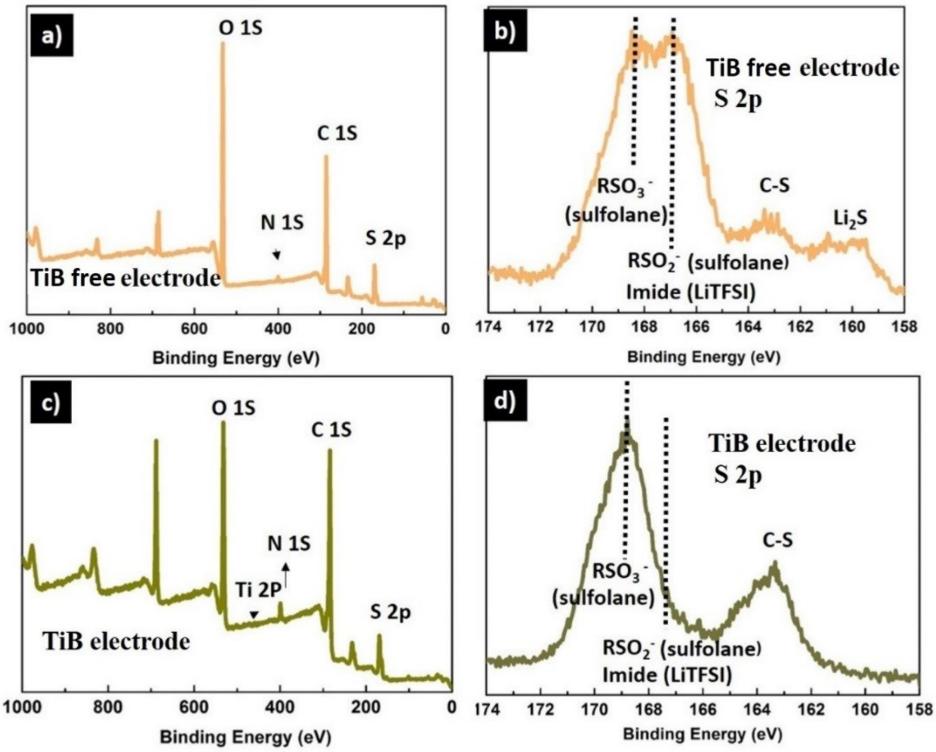

Fig. S7 XP spectra of the electrodes in the charged state after 200 cycles at 0.1 C (after the experiments shown in **Fig. 5b**): a) and c) XP survey spectra of the TiB free and TiB electrode, respectively and c) and d) high-resolution S 2p XP spectra of the TiB free and TiB electrode, respectively.

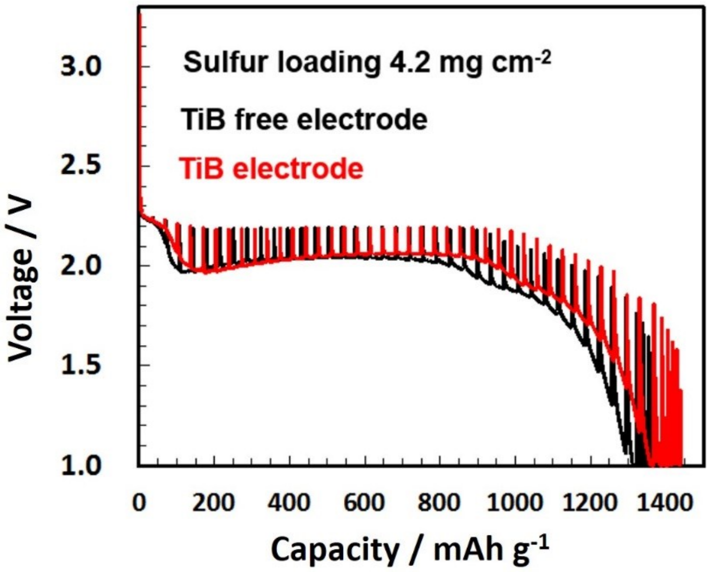

Fig. S8 GITT curves for TiB and TiB free electrodes at 0.02 C

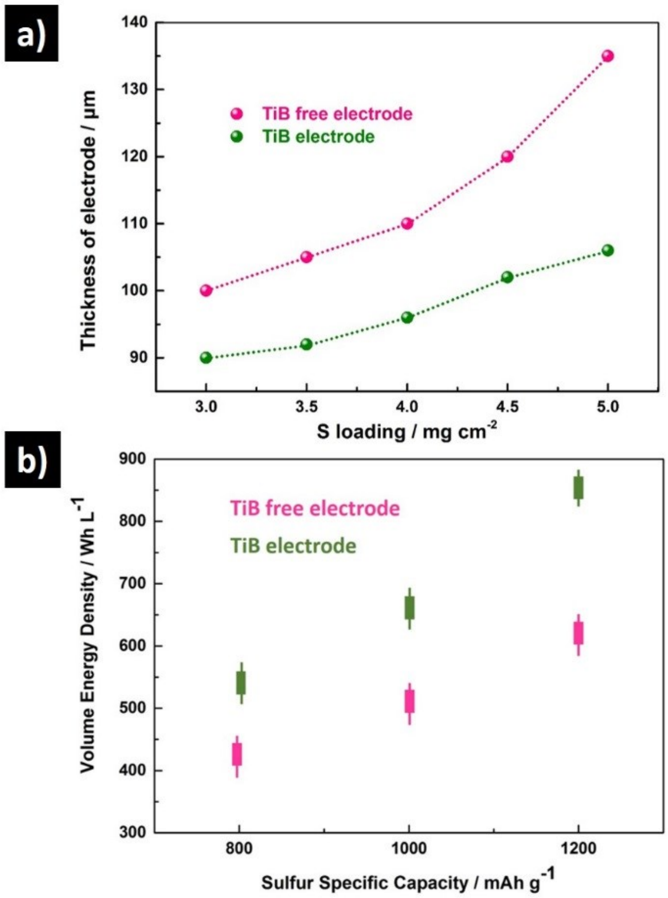

Fig. S9 a) Thickness of the TiB free and TiB electrodes under different S loadings, b) Volume energy density range of Li-S battery with the corresponding electrode thickness under S loading of 5 mg cm^{-2}. The calculation is based on 2 Ah pouch cell.

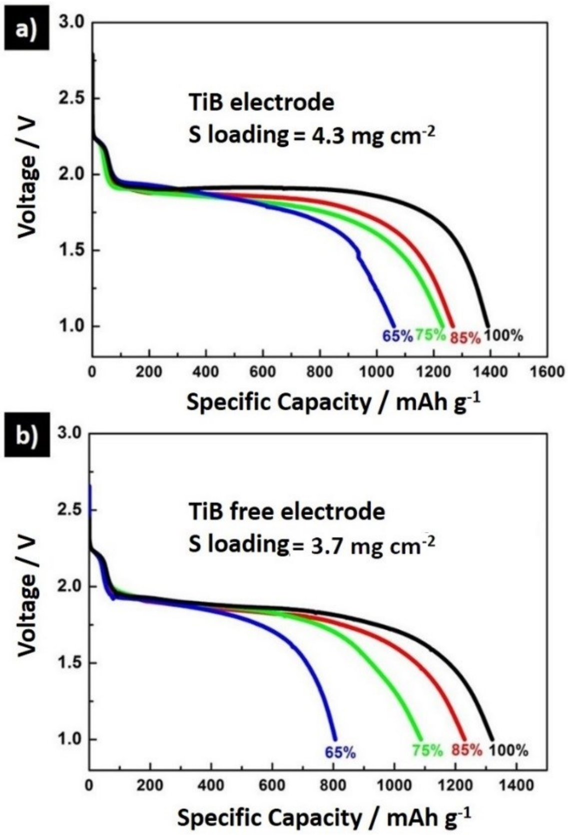

Fig. S10 Discharge curves of the compressed a) TiB electrode and b) TiB free electrode at 0.021 C with various constriction ratios relative to the initial thickness TiB free.

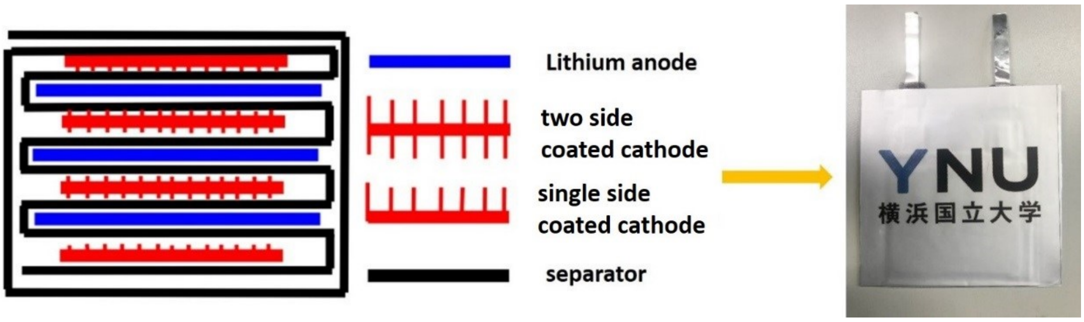

Fig. S11 Schematic representation of the internal structure of a pouch cell.

Table S3 Energy density calculations for a 2 Ah practical Li–S pouch cell.

Component	Mass (mg cm^{-2})
Cathode (Sulfur)[a]	5
Cathode current collector (Al foil)	3.4
Anode (Li metal)[b]	3.2
Anode current collector (Cu foil)	4.4
Electrolyte (E/S = 3.2)[c]	24.8
TiB additive in cathode[d]	0.16
Binder in cathode (CMC + SBR)[e]	0.19
Other (cathode/anode tap, Al package)[f]	5 wt% of the whole Li–S pouch cell
Energy density of total pouch cell[g]	305 Wh kg^{-1}

[a] The slurry coated on both sides of an Al current collector with single-side areal sulfur loading was fixed to 5 mg cm^{-2}, and the capacity delivery for the areal sulfur loading was fixed to 1200 mAh g^{-1}

[b] The theoretical consumption of lithium was calculated based on a final discharge product of Li_2S and 50 wt% excess in actual batteries

[c] The electrolyte/sulfur mass ratio was fixed to 3.2

[d] The TiB additive mass ratio in the cathode was fixed to 3 wt%

[e] The binder mass ratio in the cathode was fixed to 3.5 wt%

[f] The mass ratio of other components such as the cathode/anode tap and Al package was fixed to 5 wt% of the whole Li–S package

[g] The energy density of the 2 Ah practical pouch cell (including the mass of the Al package film)

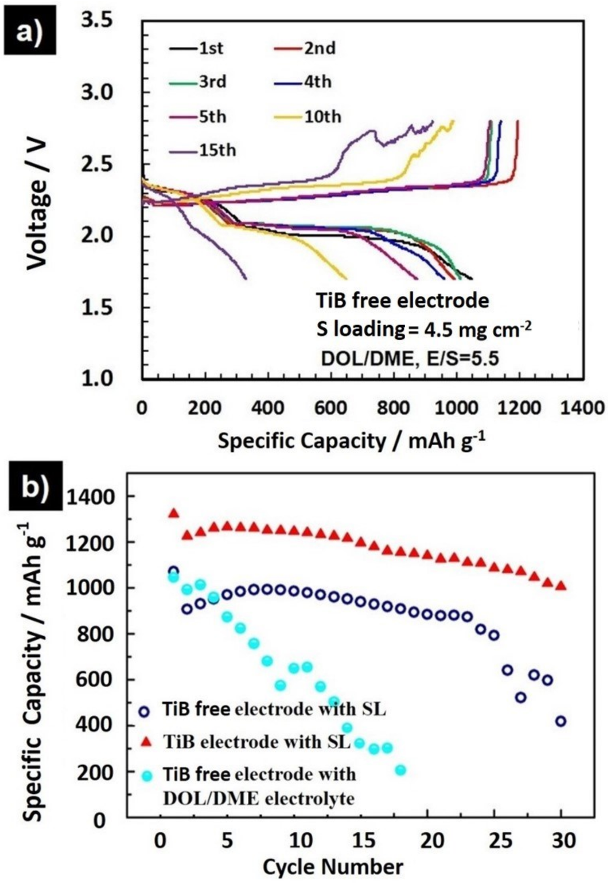

Fig. S12 a) Discharge curves of a pouch cell at 0.1 C using the TiB free electrode and DOL/DME electrolyte at an E/S ratio of 5.5. b) Cycling performance of pouch cells at 0.1 C using the TiB free and TiB electrodes at an E/S ratio of 5.5. The electrolytes were either DOL/DME or [Li(SL)$_2$][TFSA]-4HFE.

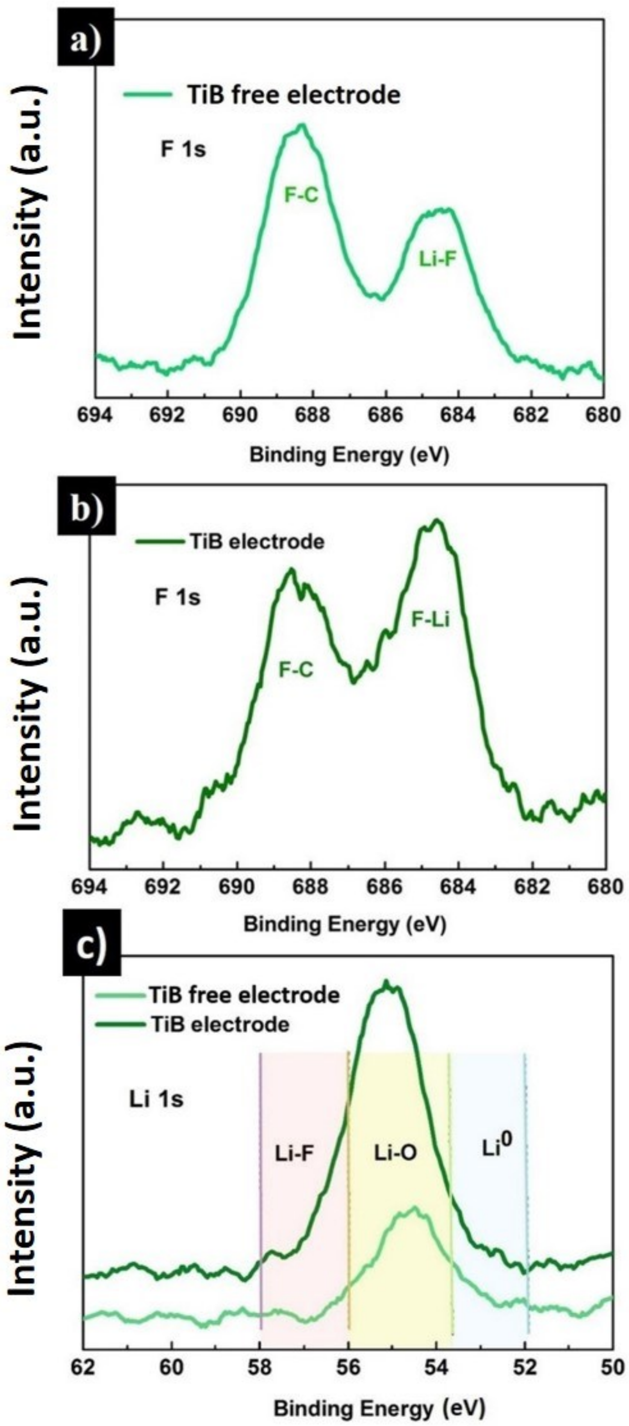

Fig. S13 XP spectra of Li anode surfaces after 30 charge/discharge cycles (**Fig. S12b**) of the TiB-free and TiB electrode pouch cells with the $[Li(SL)_2][TFSA]$-4HFE electrolyte: a), b) F 1s spectra of the TiB free and TiB electrode, respectively, and c) Li 1s spectra.

Table S4 Measured atomic compositions (%) of the lithium anode surfaces after 30 charge/discharge cycles (**Fig. S12b**) for the TiB free and TiB electrode pouch cells with the $[Li(SL)_2][TFSA]$-4HFE electrolyte.

	C	O	F	S	N	Li
TiB free electrode	61.8	22.4	1.8	0.73	1.0	12.3
TiB electrode	34.5	32.2	4.3	1.3	0.94	26.8

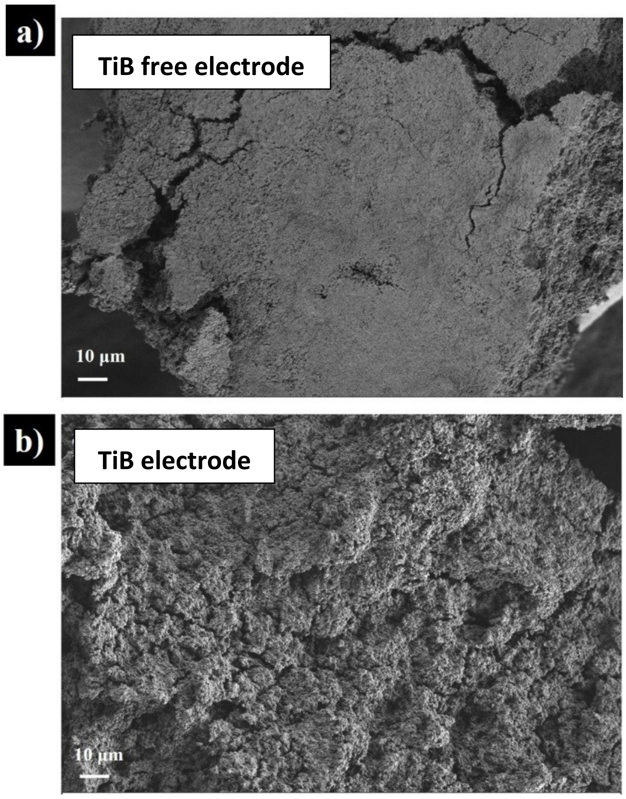

Fig. S14 SEM images of TiB free and TiB electrodes in the pouch cells.

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