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Supporting Information

An Interfacially Self-reinforced Polymer Electrolyte Enables Long-cycle 5.35 V Dual Ion Batteries

Xiaoqi Han, [1] *Huanrui Zhang,* [1] *Tianmeng Liu, Xiaofan Du, Gaojie Xu, Pengxian Han,*[*]
Xinhong Zhou, [*] *Guanglei Cui,*[*]

X. Han, Dr. H. Zhang, Dr. X. Du, G. Xu, P. Han, Prof. G. Cui
Qingdao Industrial Energy Storage Research Institute
Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences
No. 189 Songling Road, Qingdao 266101, China.
E-mail: cuigl@qibebt.ac.cn, hanpx@qibebt.ac.cn.

X. Han
Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences
Beijing 100049, China.

Tianmeng Liu, Prof. X. Zhou
College of Chemistry and Molecular Engineering
Qingdao University of Science and Technology
No. 53 Zhengzhou Road, Qingdao 266042, China.
E-mail: zxhhx2008@163.com.

Xiaoqi Han and Huanrui Zhang contributed equally to this work

Experimental section

Preparation of the PVDF/PVAc based polymer electrolyte

0.5 g mixture of polyvinylidene fluoride (PVDF, Mw=1000000) and polyvinyl acetate (PVAC, Mw=500000) with 40% PVAc content was dissolved in 10 ml acetone (AR) for 30 minutes. The solution was then poured into a teflon petri dish and placed in a fuming cupboard to form a homogeneous membrane. The membrane was thereafter punched into circular sheets with 16.5 mm in diameter and dried at 60 ^{o}C for 24 hours in vacuum. Before assembling the cell, the membrane was immersed in 1.0 M $LiPF_6$ in EMC/SL (1:4 vol: vol) electrolyte for 8 hours. For comparison, another two samples with PVAc content of 0% and 20% respectively were prepared in the same way. For the low-temperature test, the electrolyte is replaced by 1.0 M $LiPF_6$ in EMC/SL (4:1 vol: vol) to avoid electrolyte solidification. Glass fiber was served as a separator for comparison.

Electrochemical measurements

The cathode slurry was prepared by mixing graphite, super P and carboxyl methylated cellulose with a mass ratio of 90:5:5 followed by stirring in water for 4 hours and coated onto Al foil current collector afterwards. These electrodes were dried at 120 ^{o}C for 24 hours in vacuum and punched into disc sheets with 12 mm in diameter. The batteries were assembled using 2032 type coin cell in an Ar-filled glove box. Lithium metal was used as the reference and counter electrode. Galvanostatic charge/discharge measurements were conducted on a LAND CT2001A battery test system. Electrochemical impedance spectroscopy, linear sweep voltammetry and constant voltage polarization were carried out using an EC lab electrochemical work station.

The accelerated experiment was carried out as follows: 1.5 g PVAc was dissolved in 30 ml 1.0 M $LiPF_6$ in EMC/SL (1:4 vol: vol) electrolyte. The obtained solution was then poured into a H-shaped electrolytic cell which is separated by a Celgard 2400 separator. Two strip-shaped electrodes of graphite cathode and Li anode were then immersed in to the solution. The graphite cathode was polarized to 5.35 V *vs.* Li^+/Li at a scan rate of 1 mV S^{-1}, followed by a constant voltage polarization at 5.35 V *vs.* Li^+/Li for 72 hours. Then, the solution at cathode side was washed by excess methylbenzene/tetrahydrofuran mixture (anhydrous, 9:1 vol:vol) to remove the LE. The as-obtained PVAc derivative precipitate was loftdried in an Ar-filled glove box for further Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) measurement.

Characterizations

The microstructural morphology of the as-prepared membrane and cathode, as well as the energy dispersive spectroscopy, were characterized by scanning electron microscopy (SEM, HITACHI S-4800). The FTIR spectra were characterized using a Frontier FTIR spectrometer (Perkin-Elmer). X-ray diffraction (XRD) patterns was characterized with Cu k_α radiation (λ = 0.1542 nm). Raman spectra were characterized by a JY HR800 Raman spectrophotometer (Horiba Jobin Yvon, France) with 532 nm diode laser excitation. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using a 300 W Al K_α radiation. The online differential electrochemical mass spectra (DEMS, HPR-20 QIC Benthtop) measurement was carried out with a constant stream of Ar flows (1.0 ml min^{-1}) through the cell. For the DEMS measurement, the electrodes were punched into circular sheets with 16 mm in diameter. A differential scanning calorimeter (Diamond DSC, PerkinElmer DSC) ranging from -50 ^oC to 200 ^oC at 5 $^oC \cdot min^{-1}$ was conducted to evaluate the thermal stability of the as-prepared membrane. The ^{31}P and ^{19}F NMR spectra of the corresponding compound were measured using a Bruker VERTEX 70 (400 MHz) with hexadeuteroacetone as the internal reference.

DFT calculations

All quantum chemical calculations were performed by applying the DFT method with the B3LYP level and 6-31+G(d, p) basis set using Gaussian 09 program package. The structural optimization was determined by minimizing the energy without imposing molecular symmetry constraints.

MD simulations

Molecular dynamic (MD) simulations were performed on the electrolyte mixtures (SL, EMC, $LiPF_6$, PVDF and PVAC) to observe the structure changes of the electrolyte mixtures. First, the optimized electrolyte molecules were packed in a periodic box to construct the bulk systems, the compositions of simulated electrolytes are given in Table S1. The molar ratio of the electrolyte mixtures used in our simulations was SL:EMC:LiPF$_6$:PVDF:PVAC=8:2:1:4:2. Secondly, MD calculations were performed using the Forcite code with Universal force field.[1] The electrolyte mixtures system was initially relaxed in the NPT (i.e., isothermalisobaric) for 1000 ps to obtain equilibrium. The time step is 1.0 fs. Then, NVT (i.e., isothermal) MD simulations were performed for 10000ps. The temperature was controlled by a Nose-Hoover Langevin (NHL) thermostat and the pressure was controlled by a Berendsen barostat.[2, 3] The Ewald scheme and atom-based cutoff method (*i.e.*, a radius of 15.5 Å) were applied to treat electrostatic and van der Waals (vdW) interactions, respectively. [4, 5] All the partial atomic charges were defined using the Universal force field. Finally, the first-principle calculations of partial density of states were conducted using the plane-wave-based periodic DFT method in CASTEP code.[1] The electron exchange-correlation potential and the core electrons of atoms were treated by the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[6] The k-points for Brillioun zone were 0.5 Å^{-1} for bulk calculations and the cutoff energy was set to 400 eV. The convergence tolerance geometry optimization was set to 1.0×10^{-5} eV atom^{-1} for energy, 3.0×10^{-2} eV Å^{-1} for maximum force, 5.0×10^{-2} GPa for max stress and 1.0×10^{-3} Å for maximum displacement, respectively.

Table S1. Molecular dynamic (MD) simulations of electrolyte mixtures

	SL : EMC : LiPF$_6$: PVDF : PVAC 8 2 1 4 2
Number of SL per box	8
Number of EMC per box	2
Number of LiTFSI per box	1
Number of PVDF per box	4
Number of PVAC per box	2
Total number of atoms	218
Simulation box size (Å^3)	14.3×14.3×14.3
MD, density (kg/m^3)	1000
Bias temperature (K)	298

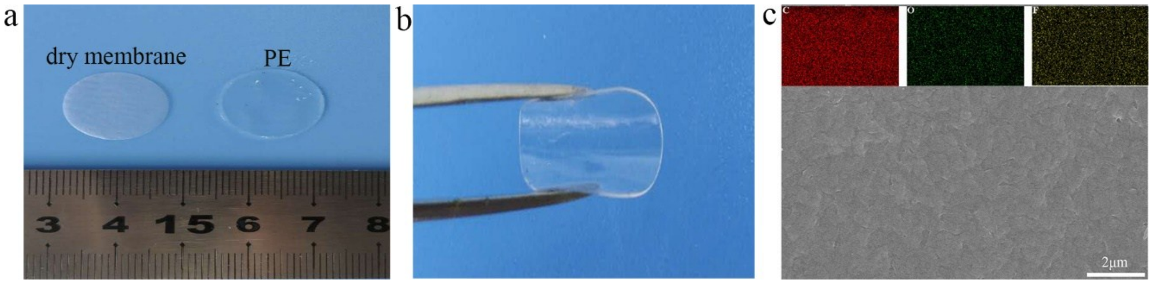

Fig. S1 Typical digital/SEM images of the as-prepared PE (40% PVAc content).

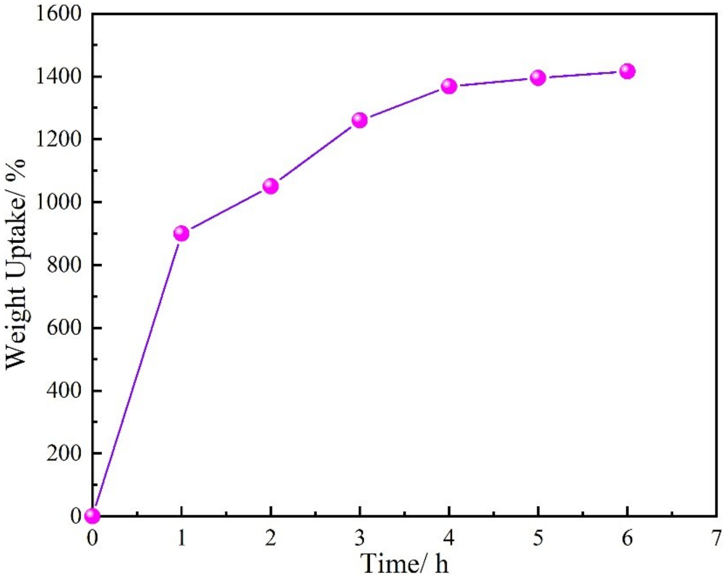

Fig. S2 The electrolyte uptake ratio versus varied immersion time for the PVDF/PVAc membrane (40% PVAc content).

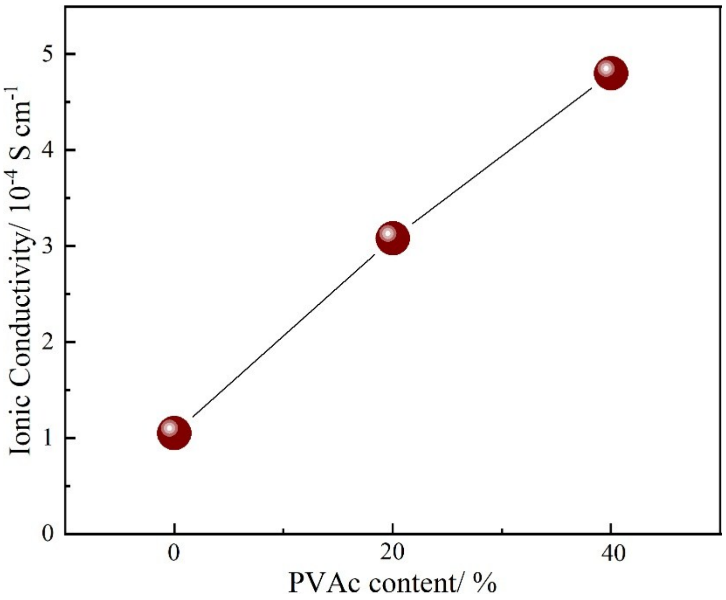

Fig. S3 Ionic conductivity comparison of the PEs with different PVAc content.

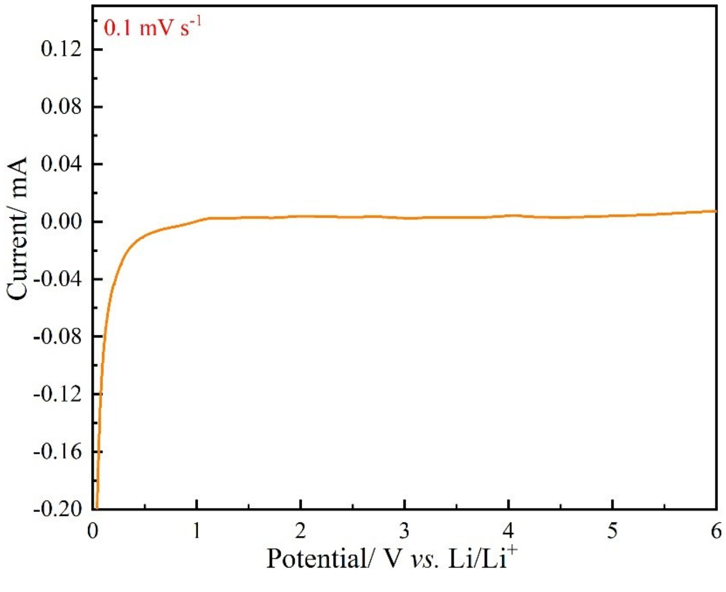

Fig. S4 The linear sweep voltammetry of the PE within 0-6 V *vs.* Li/Li$^+$ (40% PVAc content).

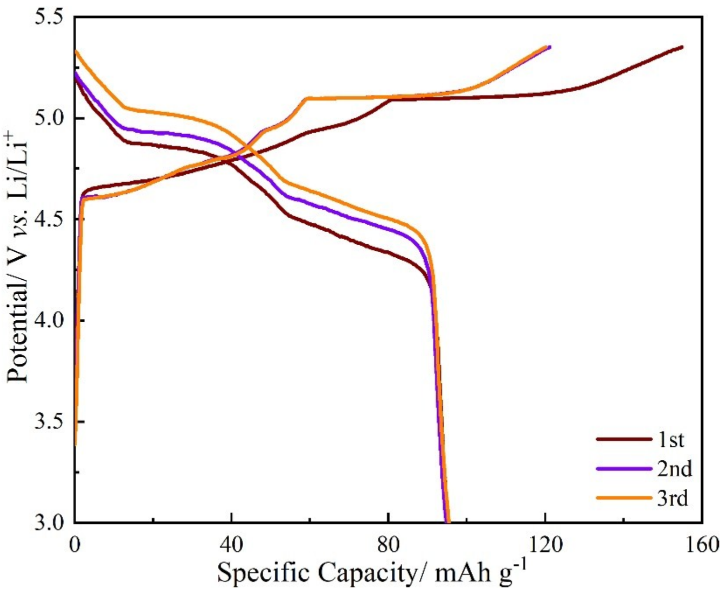

Fig. S5 The initial three charge/discharge curves of the LEDIB at 0.5 C rate.

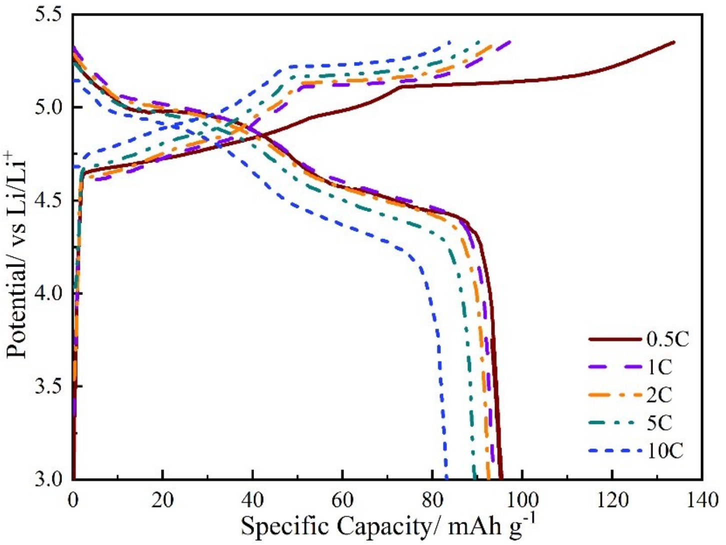

Fig. S6 The charge/discharge curves of the PDIB at varied rates (40% PVAc content).

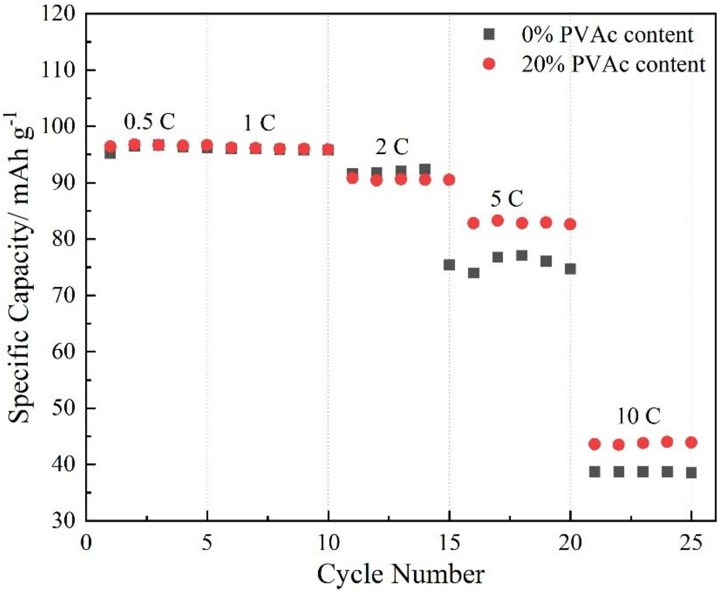

Fig. S7 Rate performances of the PDIBs with 0% and 20% PVAc content.

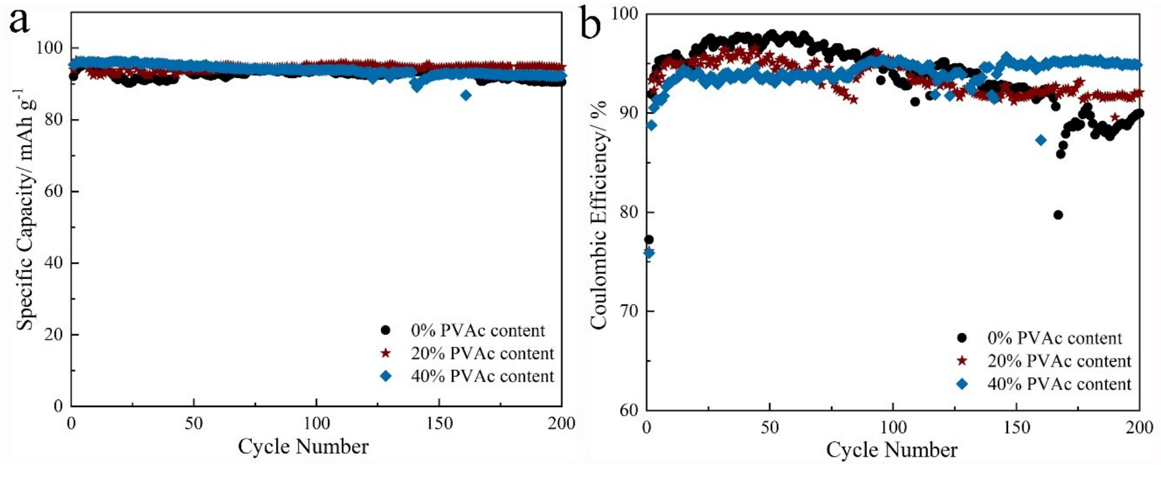

Fig. S8 a) cycle performances comparison and b) Coulombic efficiencies comporison of the PDIBs with varied PVAc content at 0.5 C rate during 200 cycles.

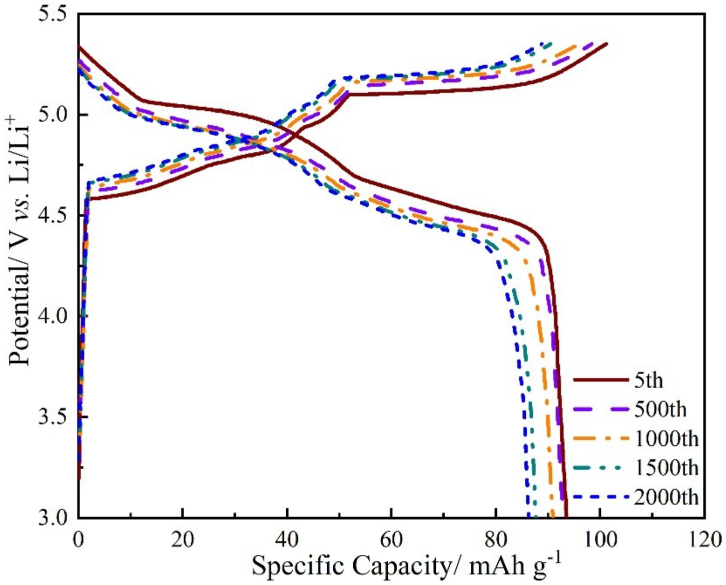

Fig. S9 The charge/discharge curves of the PDIB at different cycle numbers (40% PVAc content).

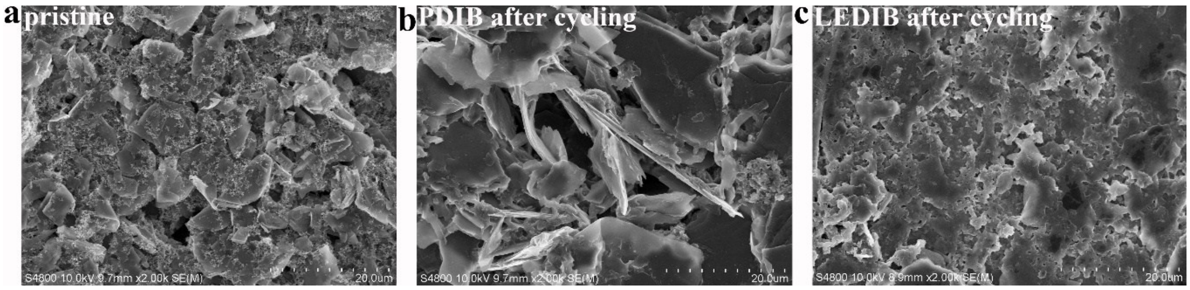

Fig. S10 Typical SEM image of the graphite cathode, a) before cycling, b) cycled in PDIB, c) cycled in LEDIB.

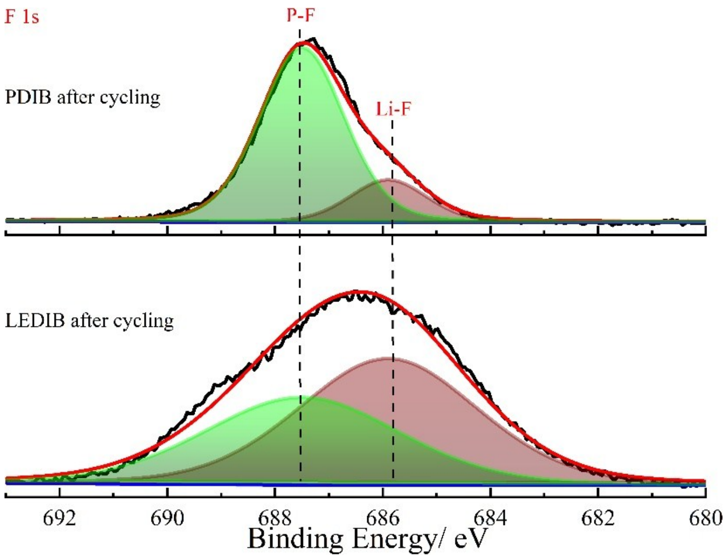

Fig. S11 The F 1s curve fittings of the cycled cathodes in PDIB and LEDIB, respectively.

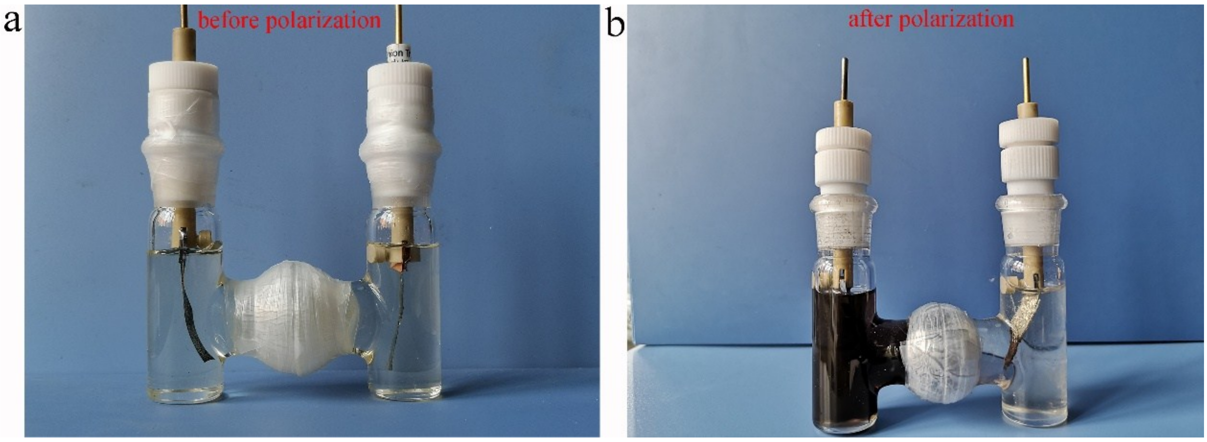

Fig. S12 Typical digital photos of the H-shaped electrolytic cell before and after constant voltage polarization.

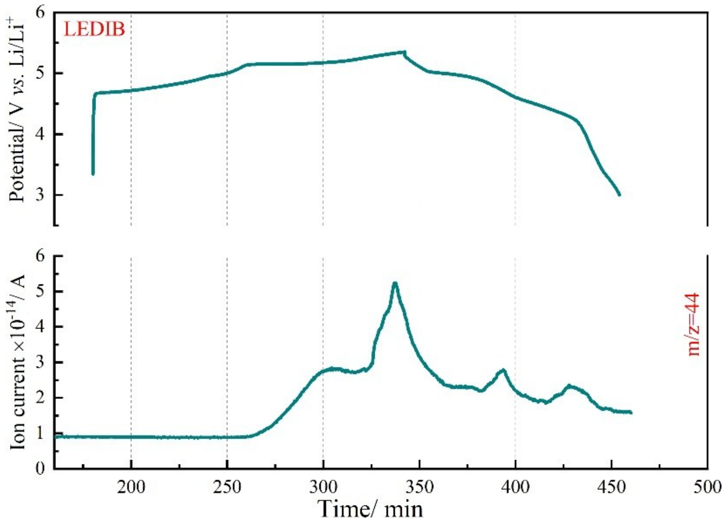

Fig. S13 The DEMS spectrum of the LEDIB during the first cycle.

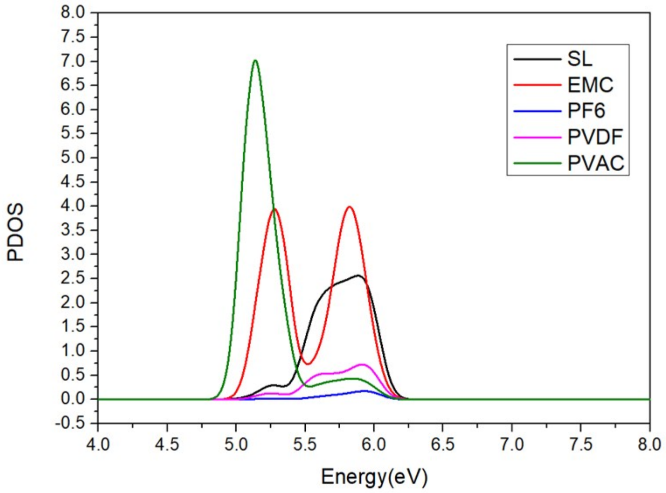

Fig. S14 Partial density of states for the PE.

Table S2. The (002) peak, interlaying spacing and the graphitization degree of the various graphite cathodes based on Figure 3e and Equation 4

Cathodes	**002/°**	**d_{002}/nm**	**G (%)**
pristine	26.48	0.3366	86
PDIB	26.44	0.3371	80
LEDIB	26.34	0.3384	65

Notes and references

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