Supporting Information for

Hybridizing Anions towards Fast Diffusion Kinetics for Tri-Ion Batteries with Significantly Improved Rate Capability and Cycling Life

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Materials and Methods

Materials. Natural graphite, Carbon doped Al foil, Al foil (thickness of 20 μm), polyvinylidene fluoride (PVDF) binder, conductive carbon black, and N-methyl-2-pyrrolidone (NMP) were purchased from Shenzhen Kejing Star Technology Ltd. Glass fiber separator (Whatman, GF/A, 47 mm in diameter), $LiPF_6$, $LiBF_4$, ethyl methyl carbonate (EMC), and vinylene carbonate (VC) were purchased from Dodochem. All the chemicals were used directly as purchased without other processing.

Electrodes Preparation. The graphite cathode was prepared by mixing 80 wt% natural graphite, 10 wt% conductive carbon black, 10 wt% PVDF binder, and moderate NMP solvent together to form a uniform slurry. Then the slurry was coated onto the Al foil and dried at 80 °C for 24 h in vacuum. Then it was punched into small circular sheets with 10 mm in diameter and the graphite loading is about 1.0~1.5 mg cm^{-2}. For the anode, Al foil was punched into circular sheets with 12 mm in diameter and directly used as the anode material. The glass fiber was also punched into circular sheets with 16 mm in diameter as a separator.

Electrolyte Preparation. 4 M hybrid electrolyte with $LiPF_6$/$LiBF_4$ complex salts dissolved in EMC and 2 wt% VC additive was prepared in a glove box (MIKRONA Universal 2440). The amount of $LiBF_4$ in the $LiPF_6$/$LiBF_4$ complex salts was set to be 0 at%, 5 at%, 10 at%, and 20 at% respectively to optimize the electrolyte.

Characterization. All the electrodes were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800), X-ray diffraction (XRD, Rigaku

Miniflex600 diffractometer with Cu Kα radiation operated at 40 kV and 15 mA), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher). The step length and scanning rate in ex-situ XRD analyses were set as 0.02° and 2° min^{-1}. Ex-situ Raman spectroscopy of the graphite cathode was analyzed using a LabRAM HR Raman spectrometer (633 nm). All the cathode and anode for ex-situ SEM, XRD, Raman and XPS measurements were washed with DMC.

Electrochemical Characterization. Graphite cathode, glass fiber separator, aluminum foil anode, and electrolyte were assembled together in the glove box to make CR2032 coin cells. Galvanostatic charge-discharge measurements and galvanostatic intermittent titration technique (GITT) measurements were performed on a battery test system (NEWARE CT-4008) at room temperature. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests were conducted using an electrochemical workstation (Autolab PGSTAT302N).

Theoretical Calculation. All calculations are performed with the Vienna ab initio simulation package (VASP),[1] using the plane-wave projector-augmented wave method[2] with an energy cut-off of 500 eV. The Perdew-Burke-Ernzerhof (PBE)[3] form of the generalized gradient approximation (GGA) was chosen as the exchange-correlation potential. Based on the convergence test, a 9×9×9 k-point grid within the Monkhorst-Pack scheme is adopted to sample the reciprocal space for the supercell with the size of 4a×4b×2c. The conjugate gradient algorithm is applied and the convergence criteria of total energy and force components are set to be 1×10^{-5} eV and 0.01 eV/Å. All the atomic positions and cell parameters were fully relaxed to obtain

reliable optimized structures and the total energy. The climbing-image nudged elastic band (CI-NEB)[4] method was chosen to calculate the energy barriers for PF_6^- and BF_4^- diffusion within the interlayer of graphite (corresponding to stage 2 intercalation process), performed in the $4a \times 4b \times 2c$ supercell.

Calculation of energy density and power density of a packaged AGTIB and DIB

Generally, the total mass of a packaged battery (M_B) is composed of 60% cathode (m_c) and anode material (m_a), and the other 40% (M_o) is composed of electrolyte, separator, current collectors, and case. Therefore,

$$m_c + m_a = 60\% \, M_B \tag{S1}$$

$$M_o = 40\% \, M_B \tag{S2}$$

In addition, the capacity of the anode is usually 10% higher than that of the cathode, which means:

$$m_a * q_a = 1.1 \, m_c * q_c \tag{S3}$$

where q_a is the specific capacity of the anode material, and q_c is the specific capacity of the cathode material.

For a dual-graphite battery, q_a is estimated to be 372 mAh g^{-1}, and q_c is estimated to be 100 mAh g^{-1}. Consequently, the mass fraction of the cathode material (R) in the battery is:

$$R = m_c \, / \, M_B = 46\% \tag{S4}$$

For an AGTIB or AGDIB, the Al foil is used directly as both the anode and current collector, which means that m_a is 0. Therefore, the mass fraction of the cathode material in the AGTIB or AGDIB (R') is:

$$R' = m_c \, /(\, m_c + M_o) = 54\% \tag{S5}$$

We denote the specific energy density based on the weight of the cathode as E_c (Wh kg^{-1}), and the specific energy density based on the weight of the total battery as E_B (Wh kg^{-1}). Therefore, the relationship between E_c and E_B is,

$$E_B = 54\% \, E_c \tag{S6}$$

where E_c can be directly obtained from the charge-discharge test results.

The power density based on the weight of the total battery (P_B, W kg^{-1}) is calculated as follows,

$$P_B = E_B / t \qquad (S7)$$

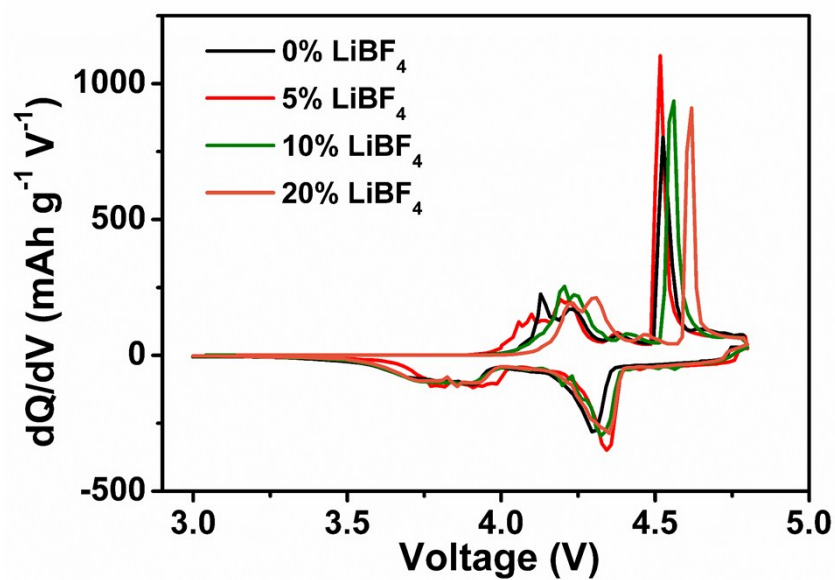where t (h) is the discharge time.

Figures and Tables

Fig. S1. dQ/dV differential curves of the AGTIBs based on electrolytes with 0%, 5%, 10% and 20% LiBF$_4$ at the 50th cycle at 2C.
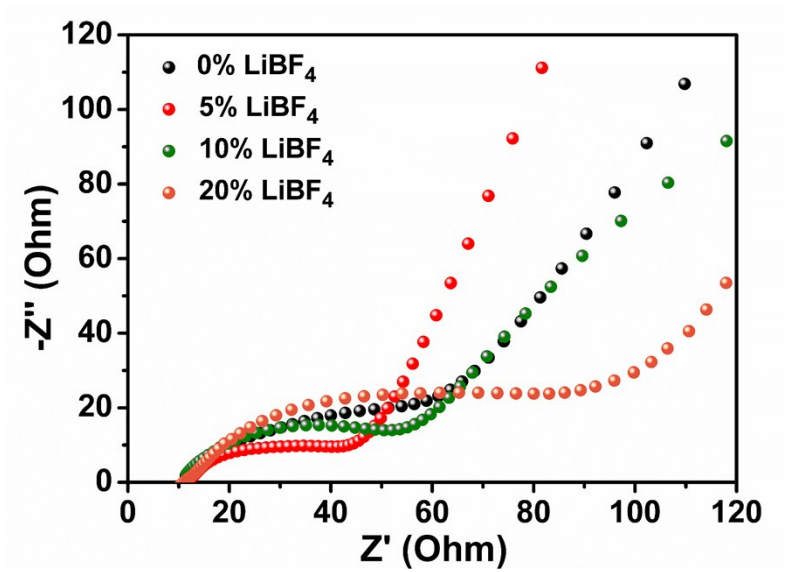
Fig. S2. Nyquist plots of the AGTIBs based on electrolytes with 0%, 5%, 10% and 20% LiBF$_4$ content after 50 cycles at 2C.
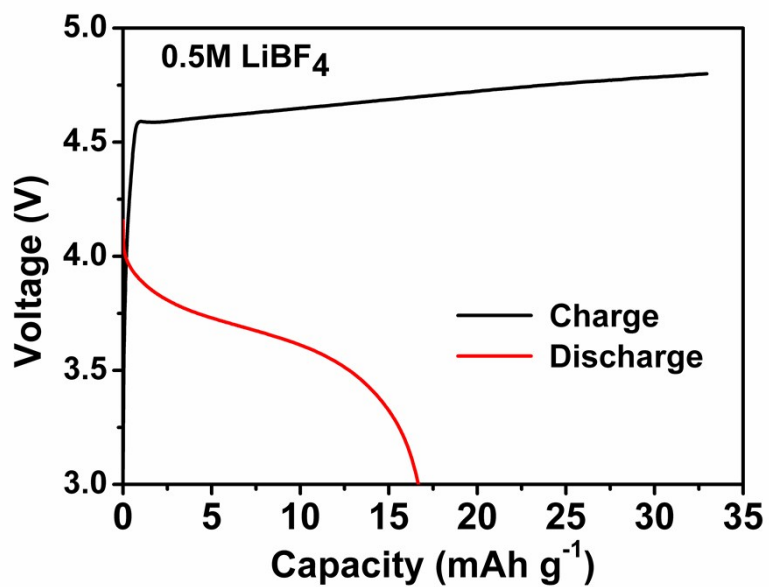

Fig. S3. Charge/discharge curves of the battery based on pure 0.5 M LiBF$_4$ electrolyte at 2C.
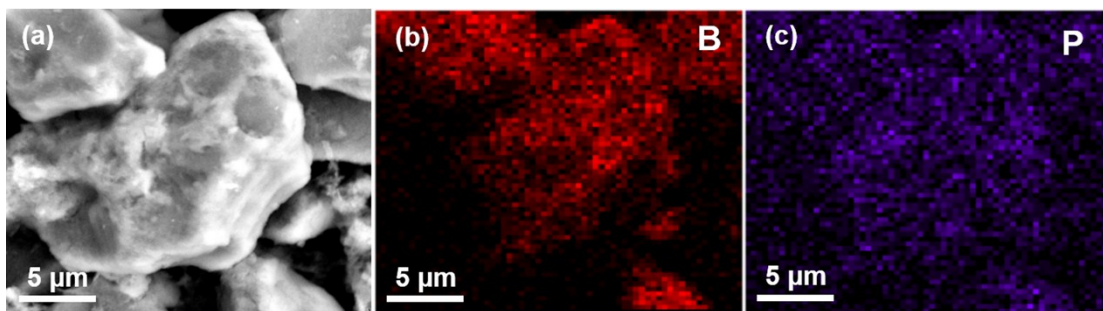
Fig. S4. EDS mapping images of B and P elements of the graphite cathode in AGTIB at fully charged state (charged to 4.8 V).
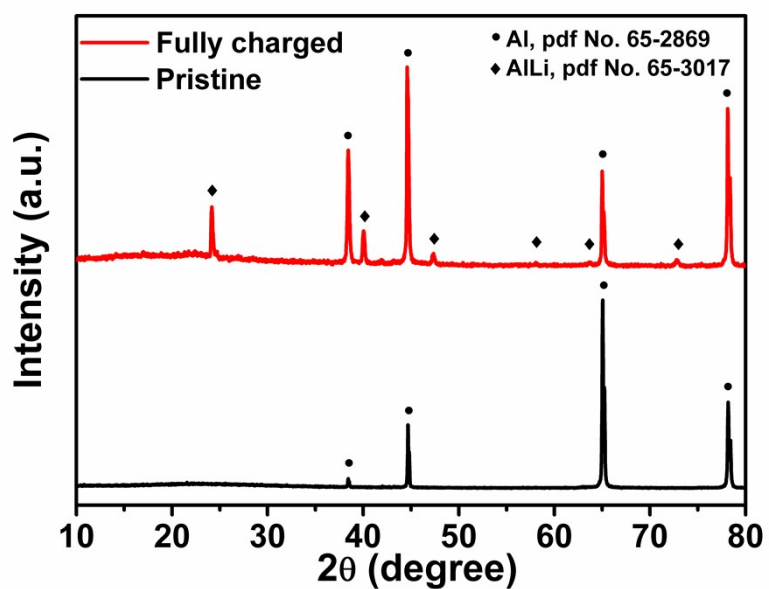

Fig. S5. XRD patterns of the pristine Al foil and the Al foil anode in the AGTIB at fully charged state (charged to 4.8 V).
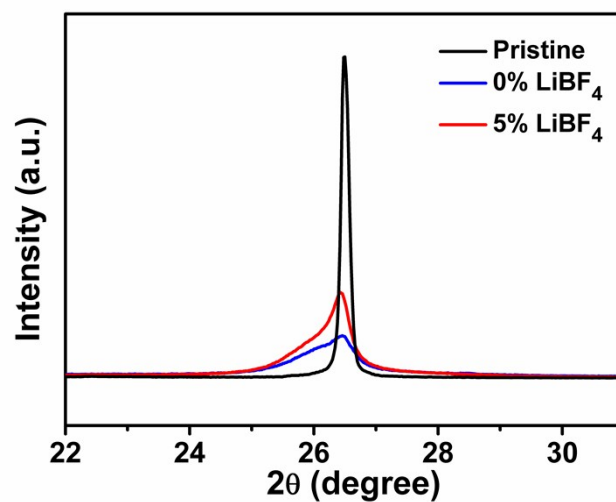
Fig. S6. XRD patterns of the pristine graphite cathode, the graphite cathode in AGTIB with 5% LiBF$_4$ after 200 cycles, and the graphite cathode in battery with 0% LiBF$_4$ after 200 cycles.
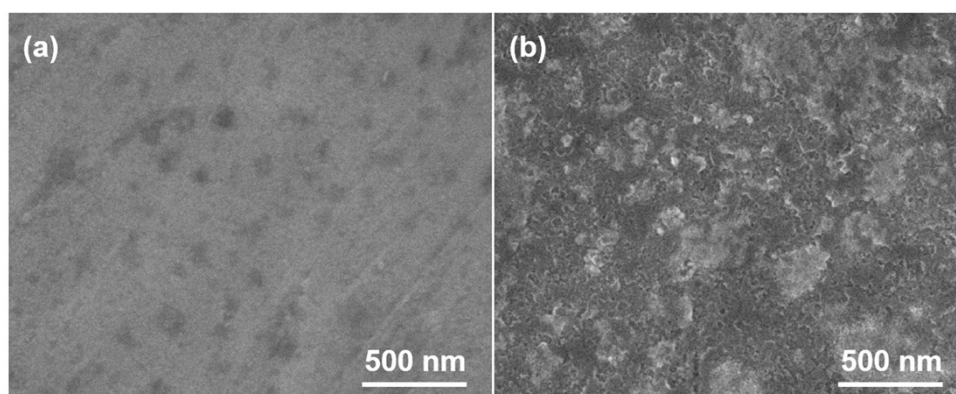

Fig. S7. SEM images of the Al foil anode in the initial state (a) and after 300 cycles (b) in the AGTIB.

Table S1. Representative electrochemical performances of the AGTIB with 5% LiBF$_4$ and battery with 0% LiBF$_4$ for comparison, which were calculated based on the mass of the graphite cathode material (C, E_c, P_c) and the packaged battery (E_B, P_B).

Current rate	AGTIB					AGDIB				
	C (mAh g^{-1})	E_c (Wh kg^{-1})	P_c (W kg^{-1})	E_B (Wh kg^{-1})	P_B (W kg^{-1})	C (mAh g^{-1})	E_c (Wh kg^{-1})	P_c (W kg^{-1})	E_B (Wh kg^{-1})	P_B (W kg^{-1})
2C	97.8	403	806	218	435	94.4	385	770	208	416
5C	97.2	400	2000	216	1080	86	349	1745	188	942
10C	94.5	389	3890	210	2101	68.6	278	2780	150	1501
15C	90.5	373	5595	201	3021	53.4	217	3255	117	1758

References

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