Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

Concentrated Electrolytes Stabilize Bismuth-Potassium Batteries

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Material and Methods

Synthesis of Bi@C anode. The Bi@C composite material was synthesized *via* carbothermal reduction of carbon-coated Bi_2S_3 nanoparticles. In a typical synthesis, 0.9702 g of $Bi(NO_3)_3$ $5H_2O$ and 0.7513 g of thioacetamide (TAA) were separately dissolved in 20 mL of ethylene glycol by bath-sonication, respectively. The TAA ethylene glycol solution was then added dropwise into the $Bi(NO_3)_3$ $5H_2O$ ethylene glycol solution under magnetic stirring. The dark brown mixture was kept stirring for 4.5 hours. The precipitate was separated by centrifugation and then was washed with deionized (DI) water and ethanol for several times prior to overnight vacuum-drying at 80 ℃. The products are recognized as Bi_2S_3 nanoparticles by XRD and SEM. 100 mg such Bi_2S_3 nanoparticles were dispersed in a Tris-buffer solution (10^{-2} M) containing 50 mL of DI water and 50 mL of ethanol by bath-sonication for 5 minutes. 150 mg of dopamine hydrochloride was subsequently added. The mixture was bath-sonicated for another 10 minutes and then was kept stirring at room temperature for 24 hours. After centrifugation, solid powders were separated and washed with DI water for several times, followed by a vacuum-drying process at 80 ℃ overnight. The as-prepared solid powders were subsequently annealed at 350 ℃ for 3 hours and then at 650 ℃ for another 4 hours in an Ar atmosphere with a temperature ramping rate of 3 ℃/min. The final products are confirmed as Bi@C core-shell nanoparticles by XRD, SEM and TEM characterizations.

Materials Characterization. The structure and purity of the as-synthesized Bi@C anode were analyzed using a Rigaku Miniflex 600 or Ultima IV powder X-ray diffractometers (XRD) with CuKα radiation at a voltage of 40 kV and current of 15/40 mA. For ex-situ XRD studies, batteries were (de)potassiated to a preset voltage and disassembled presently in an argon-filled glovebox (Vigor, H_2O < 0.1 ppm, O_2 < 0.1 ppm). Afterwards, the bulk anodes were washed with DME for three times to remove the attached electrolyte salt, and subsequently sealed with Kapton tapes for XRD characterization. Thermogravimetric analysis (TGA) was performed on Netzsch STA449F3 with a temperature ramp of 10 ℃/min under air flow. The microscopic features and energy-dispersive X-ray (EDX) element mapping of the Bi@C anode were characterized on a field-emission scanning electron microscope (FESEM, HITACHI SU-8010) and transmission electron microscope (TEM, HITACHI). The bulk anode including Bi@C materials, carbon black and CMC binder was directly peeled from Al current collectors for the Brunauer–Emmett–Teller (BET) measurement which was performed on a Micromeritics ASAP 2020 instrument.

Electrochemical Characterization. All batteries were fabricated and tested in half-cell configurations. Electrodes were fabricated based on a slurry-coating method. Firstly, active materials (Bi@C) and Super P carbon black were thoroughly mixed with a weight ratio of 80:10 through grinding. Then, the above mixtures were further mixed with a binder (carboxymethyl cellulose, CMC) at a weight ratio of 90:10 by using DI water as the dispersing medium. After overnight stirring, the slurry was cast on an Al foil by the doctor-blading technique and dried under vacuum at 80 ℃ overnight. CR2032-type coin cells were assembled in an argon-filled glovebox with oxygen and water content lower than 0.1 ppm. Potassium metal foils were used as counter and reference electrodes while glass fibers (Grade GF/F, Whatman, USA) were applied as separators. 1 M, 3 M, 5 M, 7

M KTFSI-DEGDME or 0.8 M KPF_6-EC-DEC-10% FEC were used as electrolytes. The cells were galvanostatically charged/discharged between 0.1 and 1.5 V versus K/K^+ at various current densities on Land CT2001 battery-testers. The specific current density was set based on the mass of Bi@C anode. The specific capacity was calculated based on the weight of the Bi@C anode if not specified. Linear sweep voltammetry curves (LSV) were recorded on a Bio-Logic SP-300 electrochemical workstation at a scanning rate of 0.2 mV/s with batteries in which K foils were used as counter and reference electrodes while Al foils were applied as working electrodes. Electrochemical impedance spectroscopy (EIS) was acquired by applying a sine wave with amplitude of 10 mV over a frequency range from 100 kHz to 10 mHz on a Bio-Logic SP-300 electrochemical workstation. Galvanostatic intermittent titration technique (GITT) was conducted on a Land CT2001 instrument with current pulses of 1 hour at a rate of 10 mA/g followed by a rest interval for 6 hours, and the process was repeatedly performed until the cell voltage reached 0.1 V or 1.5 V (vs. K/K^+). Prior to GITT tests, all the batteries were galvanostatically cycled once at 10 mA/g for activation. The K-ion diffusion coefficients ($D_{K\text{-}ion}$) were calculated from the GITT data by the following formula first outlined by Weppner and Huggins:[S1]

$D_{K\text{-}ion} = (4/\pi\tau)*[n_M V_M/S]^2*[\Delta E_s/\Delta E_t]^2$

Here, τ is the constant current pulse duration; n_M and V_M are the mole number and mole volume of the active materials, respectively; S represents effective contact area of electrolyte and active materials, which is estimated to be the Brunauer–Emmett–Teller (BET) surface area of the bulk electrode here; ΔE_s and ΔE_t are the change in the steady-state voltage and overall cell voltage upon applying a current pulse in a single step GITT experiment, respectively.

Reference:

S1. W. Weppner, R. A. Huggins, *J. Electrochem. Soc.*, 1977, **124**, 1569-1578.

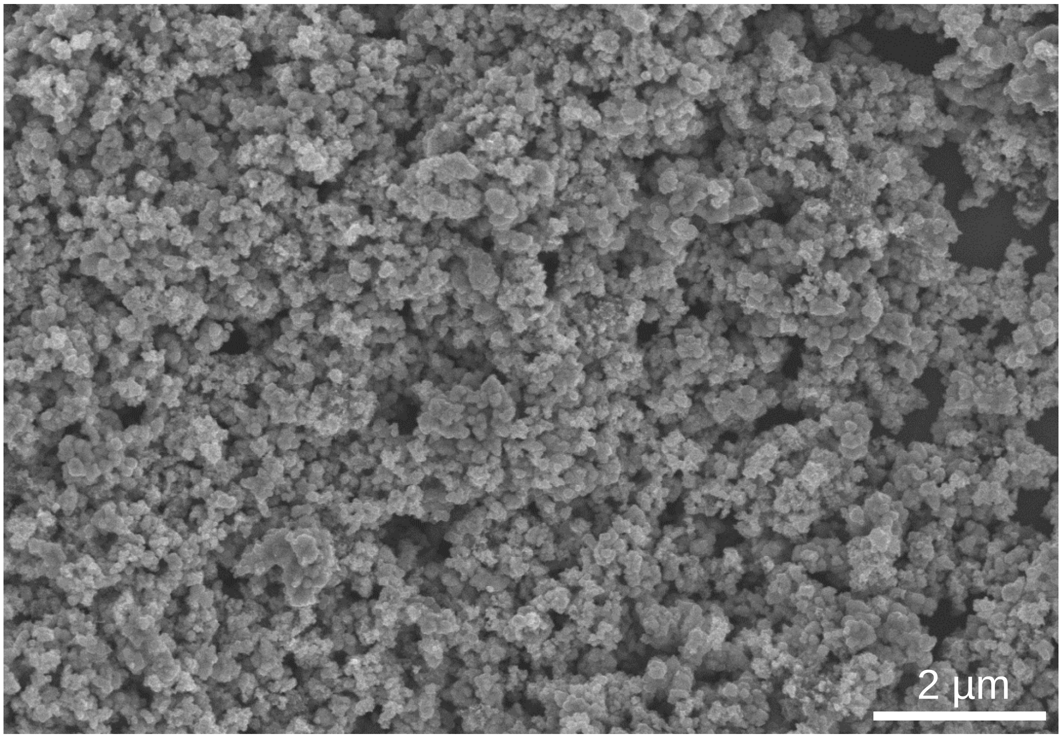

Figure S1. SEM image of the as-synthesized Bi@C nanocomposite material.

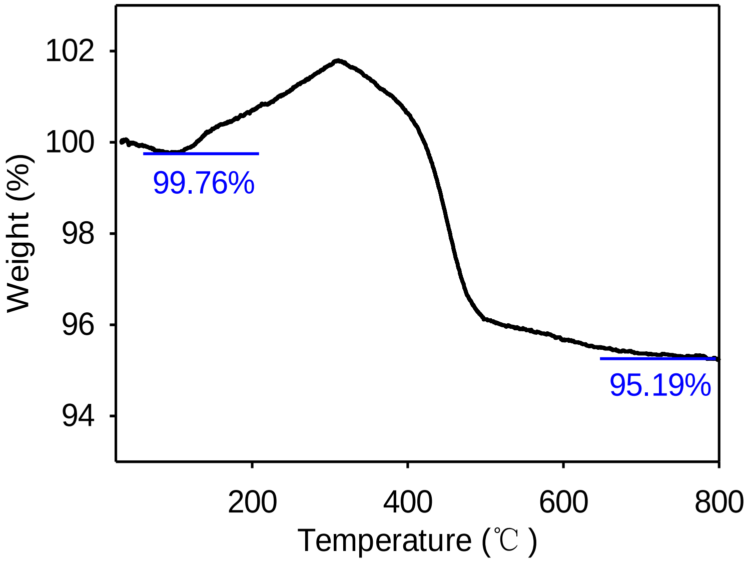

Figure S2. Thermogravimetric analysis (TGA) of Bi@C nanocomposite. The content of Bi and C are calculated to be 85.59 wt% and 14.41 wt%, respectively.

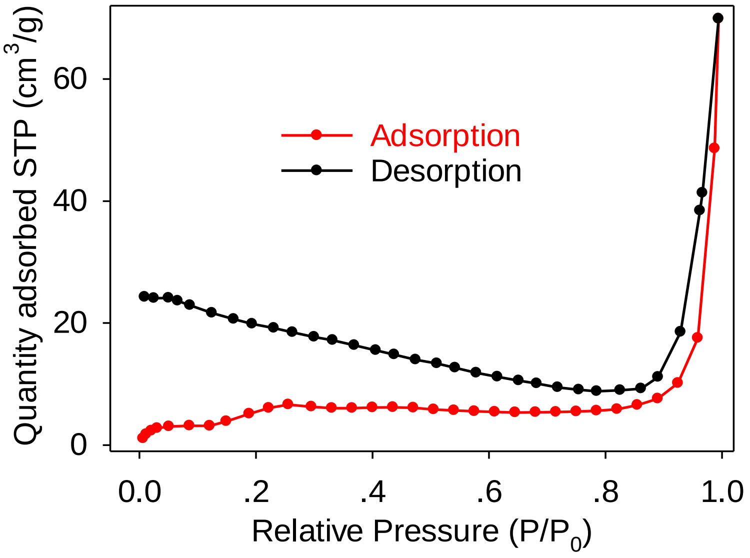

Figure S3. Brunauer–Emmett–Teller (BET) measurements of bulk Bi@C anode together with carbon black and CMC binder (directly peeled from Al current collectors) generate a specific surface area of 24.7 m^2/g.

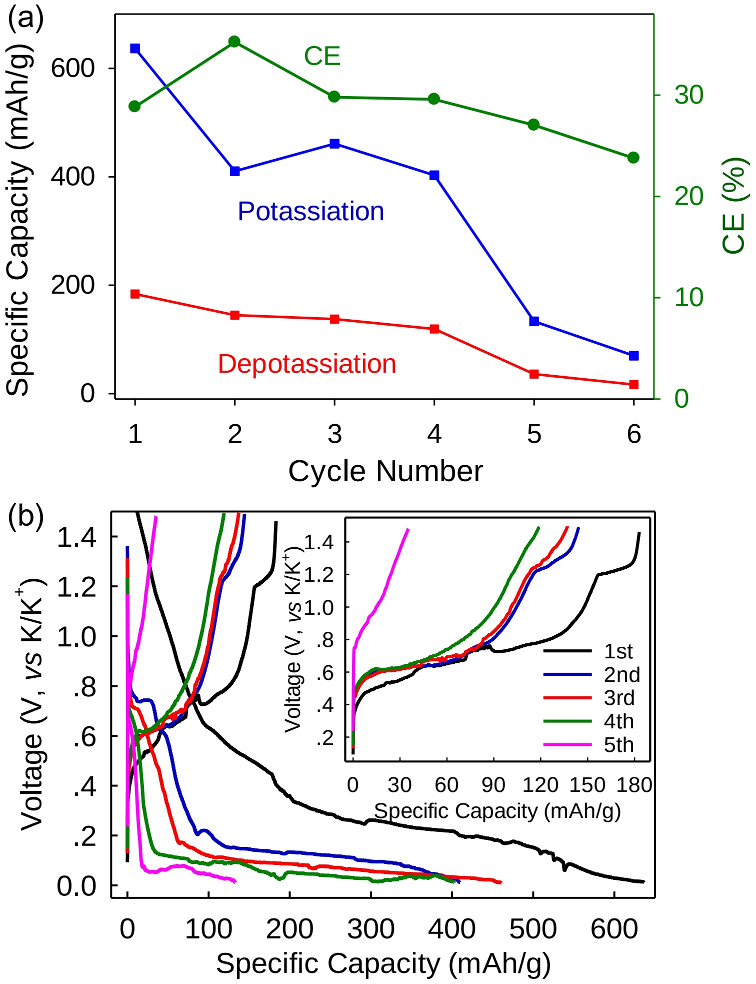

Figure S4. Electrochemical cyclability (a) and voltage profile (b) of Bi@C anode with 0.8 M KPF_6-EC-DEC-10% FEC electrolyte at a rate of 10 mA/g.

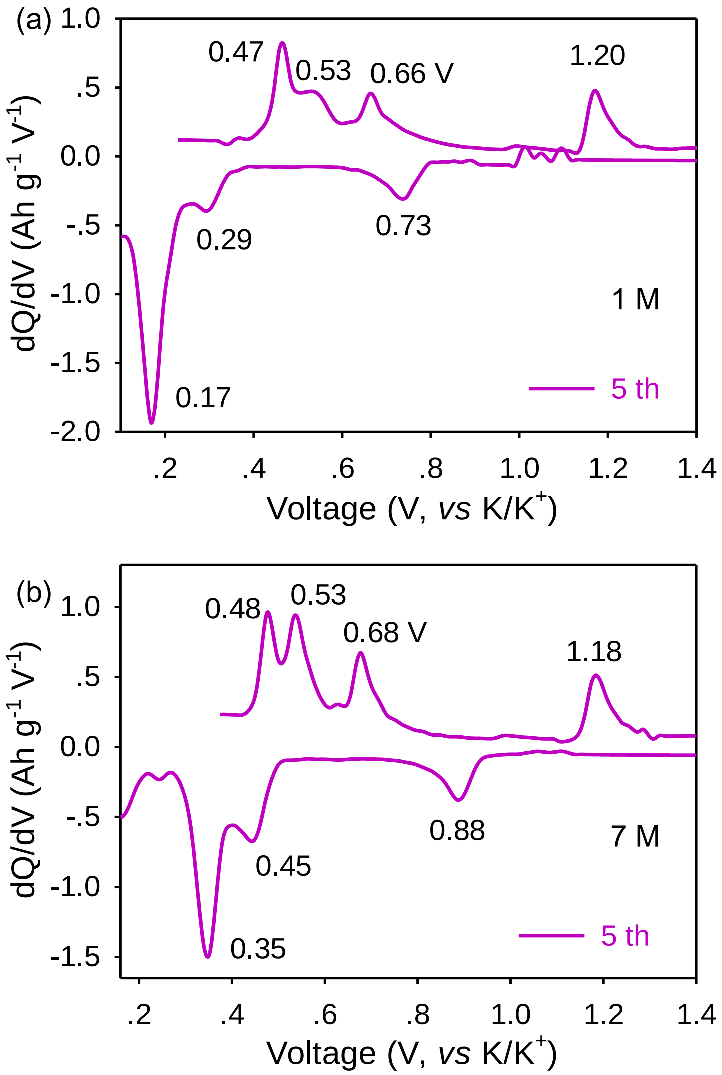

Figure S5. The corresponding 5th cycle dQ/dV curves in the 1 M (a) and 7 M (b) KTFSI-DEGDME electrolytes at 10 mA/g.

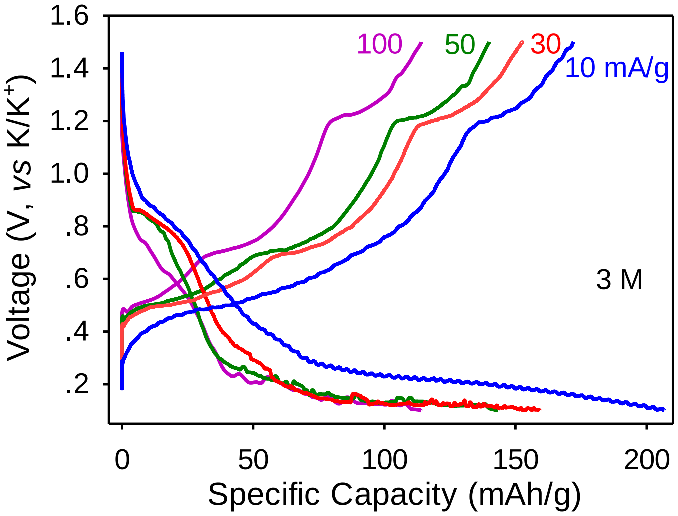

Figure S6. Rate capability of Bi@C anode in the 3 M KTFSI-DEGDME electrolyte.

	R_s (Ω)	R_f (Ω)	R_{ct} (Ω)
Initial	16.3	-	2719
After 3-cycle	11.77	10.3	408.9

Figure S7. Resistance derived from electrochemical impedance spectroscopy. R_s: electrolyte resistance; R_f: contact resistance; R_{ct}: charge transfer resistance.

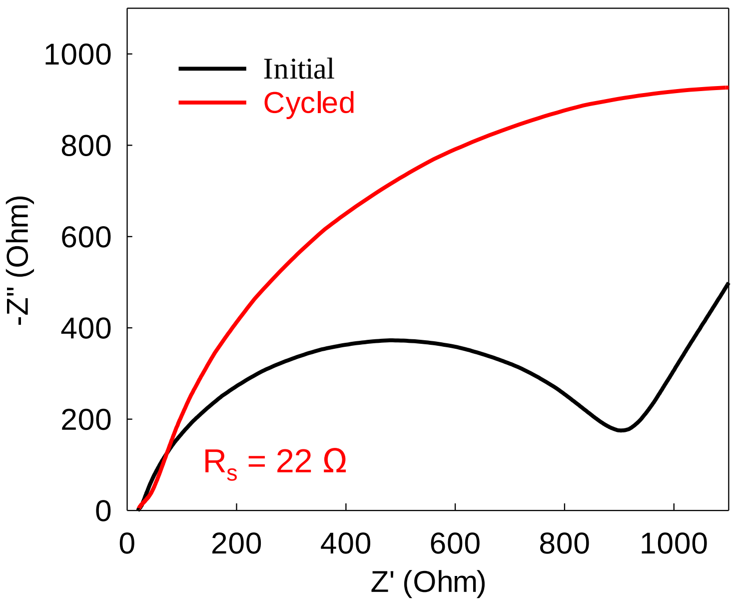

Figure S8. EIS curves of initial and cycled Bi@C anode in the 7 M KTFSI-DEGDME electrolyte.