

Supporting Information:

**Electrochemically Captured Zintl Clusters Induced
Bismuthene for Sodium-ion Storage**

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Experimental Procedures

Chemicals. The Bi sheet ($10 \times 10 \text{ mm}^2$, 99.9%), Pt sheet ($10 \times 10 \text{ mm}^2$, 99.99%), electrode materials were obtained from Alfa-Aesar. Tetrabutylammonium hexa-fluorophosphate (TBAP, >99%), tetramethylammonium hexa-fluorophosphate (TMAP, >99%) and tetraethylammonium hexa-fluorophosphate (TEAP, >99%) were also obtained from Alfa-Aesar and dried at room temperature in a vacuum oven for 12 h before use. N, N-Dimethylformamide (DMF, anhydrous, amine free, 99.9%) was purchased from Alfa-Aesar and solvents were freshly distilled by CaH_2 prior to use.

Instrumentation. Atomic force microscopy (AFM) measurements were carried out on a Bruker multimode-8 scanning probe microscope. The X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV X-ray diffractometer in the 2θ range of 10° - 80° with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, scan rate of $10^\circ \text{ min}^{-1}$). The Raman spectrum was conducted on a confocal Raman spectrometer (WITec Alpha-300R, 532 nm). Morphology and microstructure of the prepared samples were characterized by using transmission electron microscopy (TEM, JEOL, Shanghai Chenmai Co., Ltd.). ESI-MS has been performed on a Thermo Finnigan LCQ ADVANTAGE MAX ion trap mass spectrometer in the negative ion mode: Spray voltage 3.66 kV, capillary temperature 290°C , capillary voltage -20 V, tube lens voltage -121.75 V, sheath gas flow rate 45 arb, sweep gas flow rate 7 arb. The compounds in electrolyte solution after reaction of Bi in DMF solutions of TBAP was measured with gas chromatogram (Agilent GC-MS 7890A/5975C).

Preparation of Bi. All electrochemical processes were carried out in a H-type cell using a DC power supply (LW10J2, Shanghai LiYou Electric Co., Ltd) with Ar atmosphere. Different

samples were fabricated in DMF of 0.1M TAMP/ TEAP/ TBAP respectively as an electrolyte under -5V for 6 hours. The obtained products were immediately collected by centrifugation at 10000 rpm, subsequently washed with DMF and ethanol, and then dried under vacuum at room temperature.

Electrochemical measurements.

The dried Bi powder prepared in the DMF solution of TEAP/TBAP was mixed with a binder poly(vinylidene fluoride) (PVDF) and acetylene black at weight ratios of 80 : 10 : 10 in N-methyl-2-pyrrolidone (NMP) solvent to form a slurry. Then, the slurries were uniformly pasted on an Al foil with a blade. These prepared electrode sheets were dried at 80 °C in a vacuum oven for 12 h and pressed under a pressure of approximately 20 MPa. CR2016-type coin cells were assembled inside an MBraun glove box ($H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm) using the metallic sodium counter/reference electrode, a polypropylene separator (Celgard 2400), an electrolyte of 1M $NaPF_6$ in diglyme. Galvanostatic charge–discharge cycles at 100 mA g^{-1} were carried out with an Arbin battery cycler (BT2000) between 2.0 and 0.01 V vs. Na^+/Na .

Results and Discussion

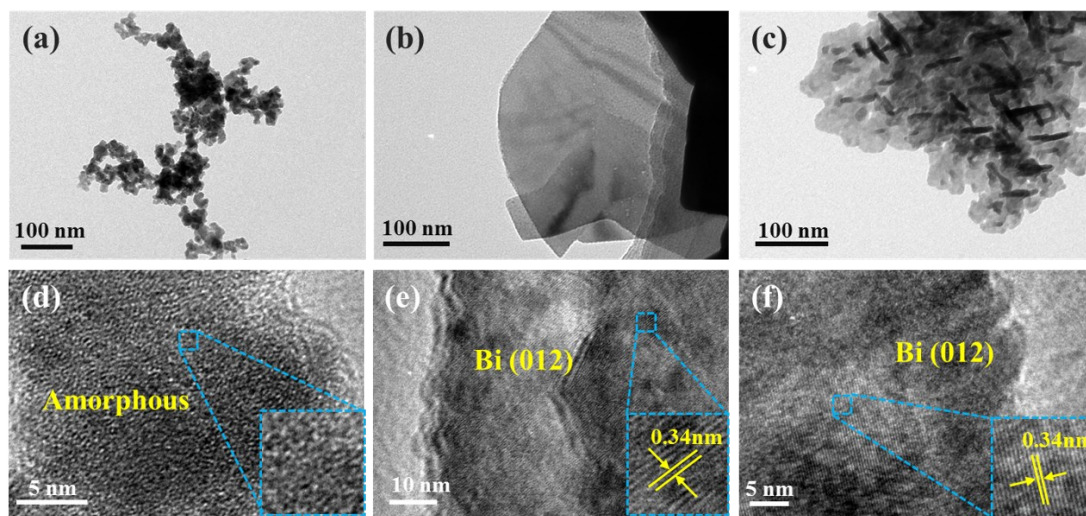


Figure S1. (a-c) TEM images, (d-f) HETEM images and of BNs-TMAP, BNs-TEAP, BPs-TBAP.

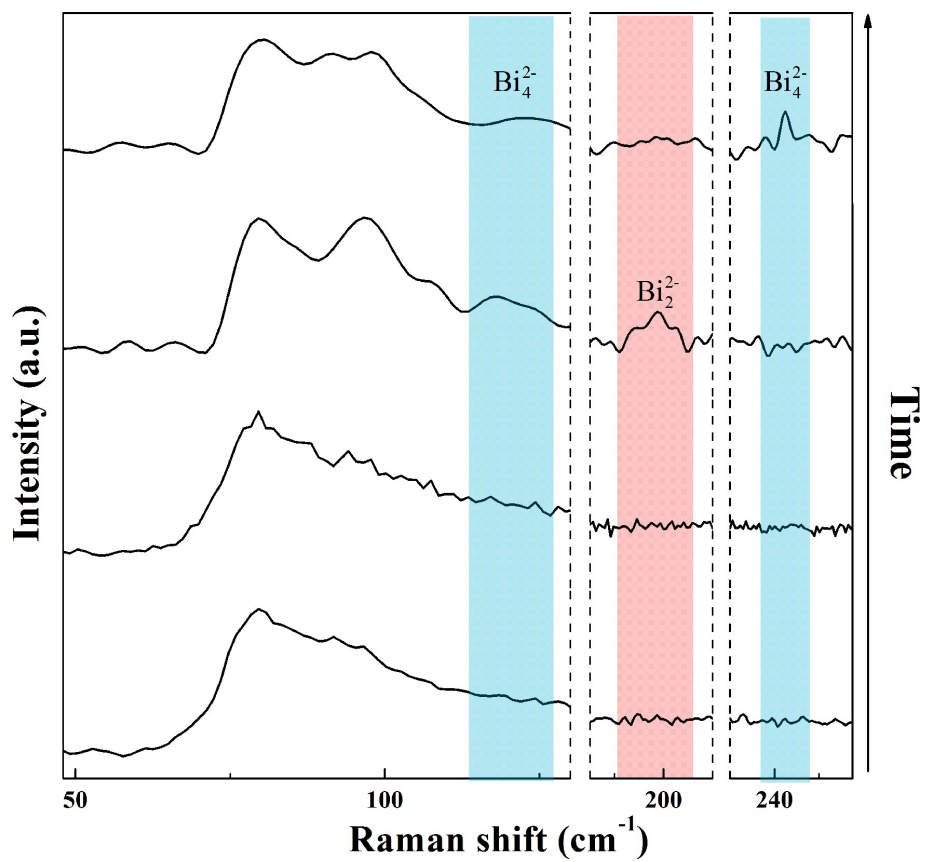


Figure S2. In-situ Raman spectra of $(\text{TMA}^+)_2\text{Bi}_2^{2-}$.

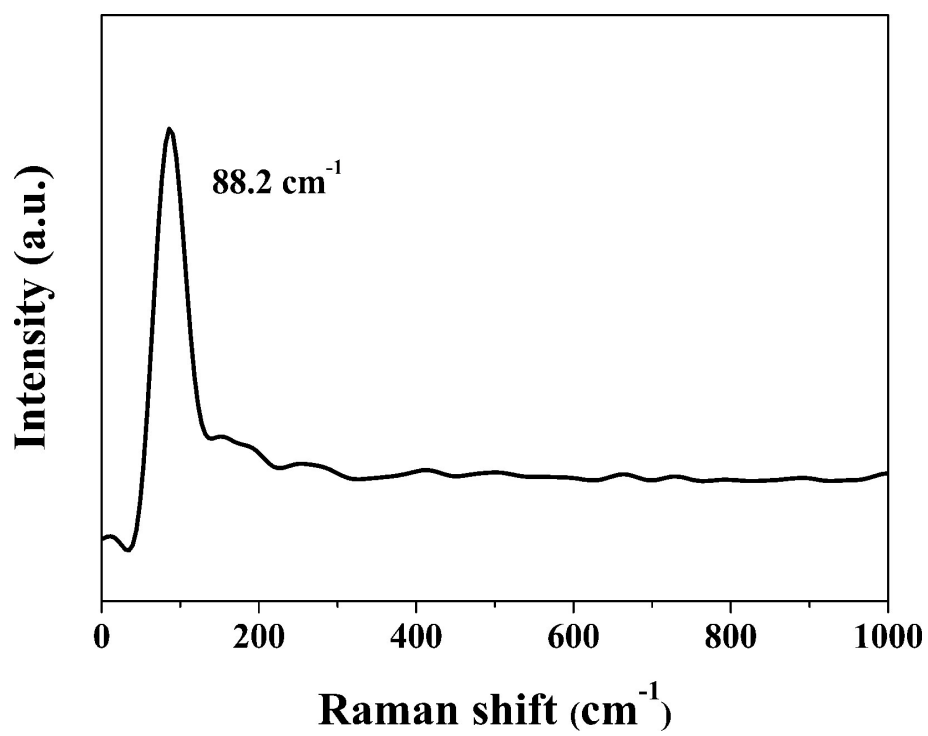


Figure S3. Raman spectra of bulk Bi.

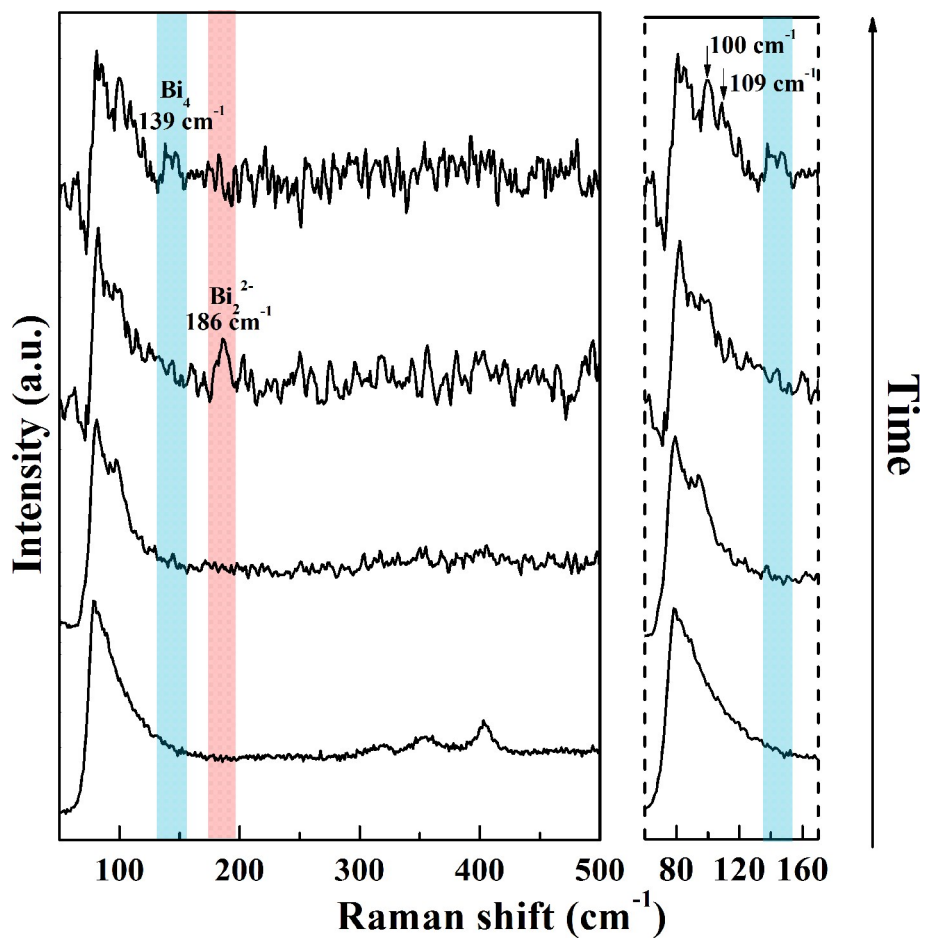


Figure S4. In-situ Raman spectra of $(\text{TBA}^+)_y\text{Bi}_x^y$.

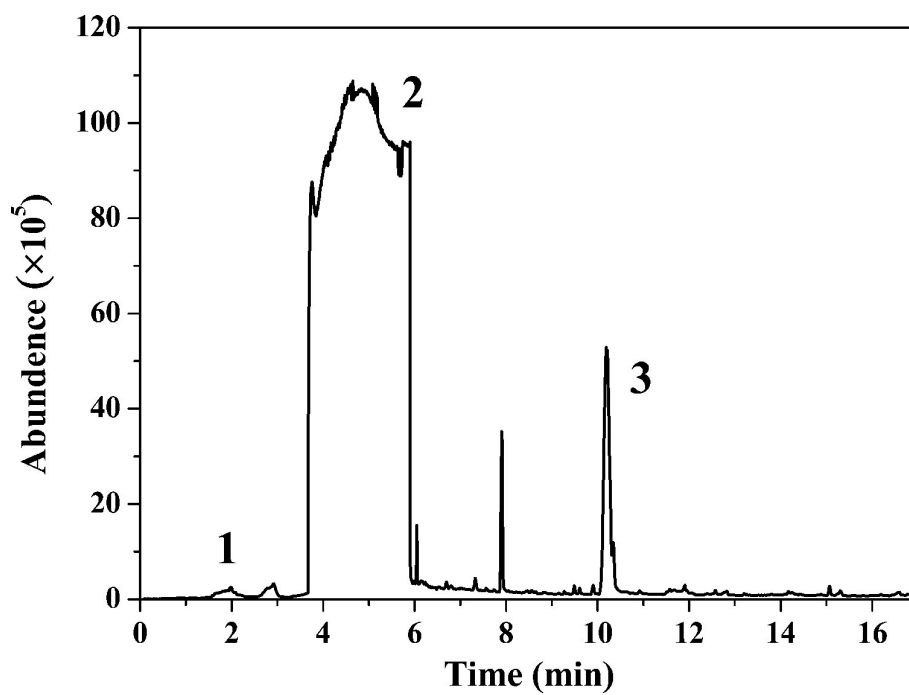


Figure S5. GC-MS spectra of TBAP electrolyte after reaction.

Table S1. Identification of TBAP electrolyte after reaction

Label	Compound
1	Butene
2	DMF
3	Tributylamine

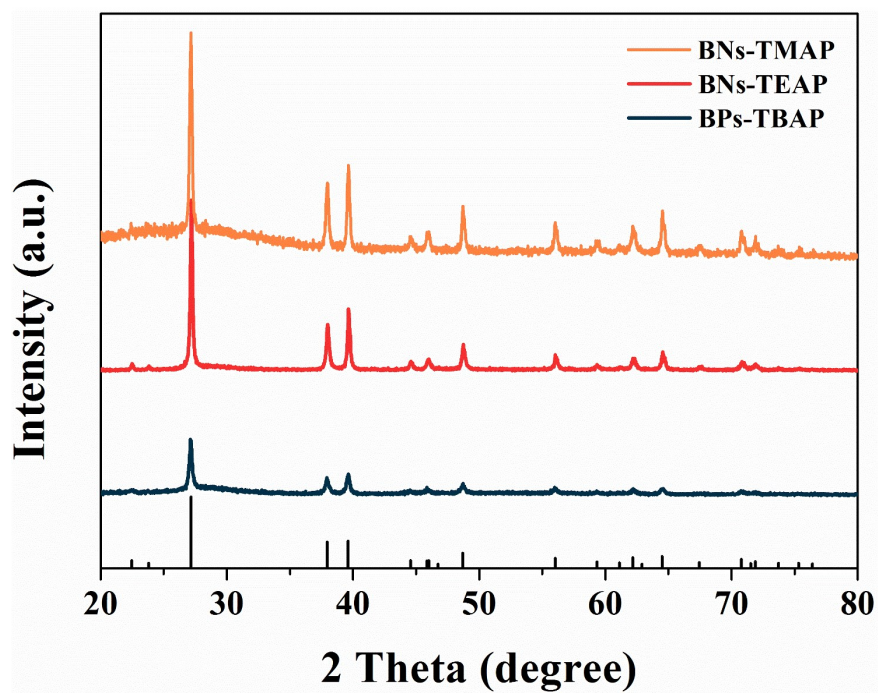


Figure S6. XRD pattern of BNs-TMAP, BNs-TEAP, BPs-TBAP and PDF card (PDF#44-1246).

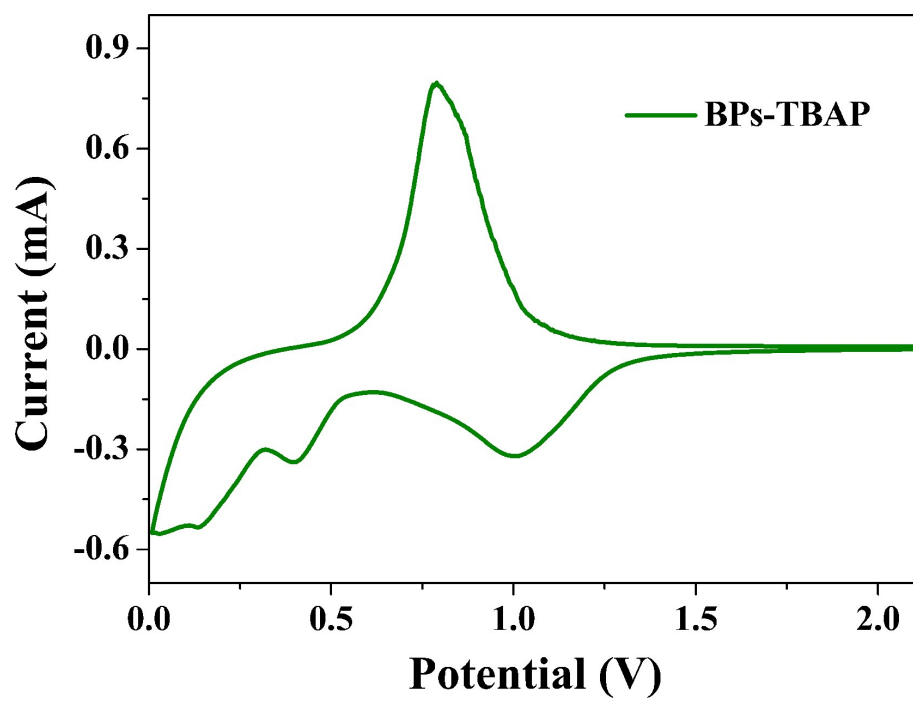


Figure S7. The CV curve of BPs-TBAP.

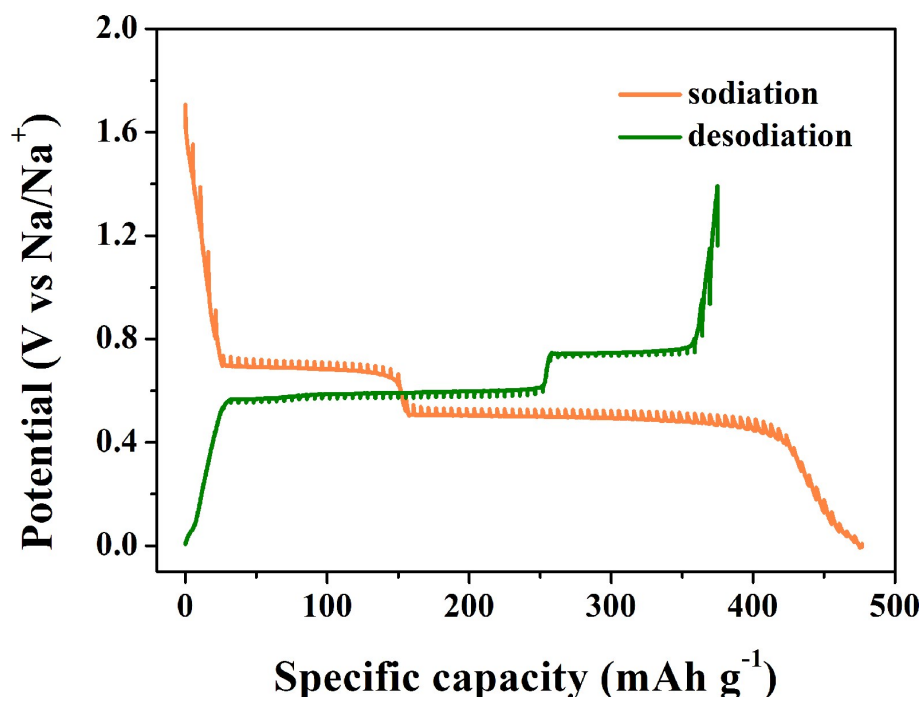


Figure S8. The quasi-equilibrium voltage curve from GITT.

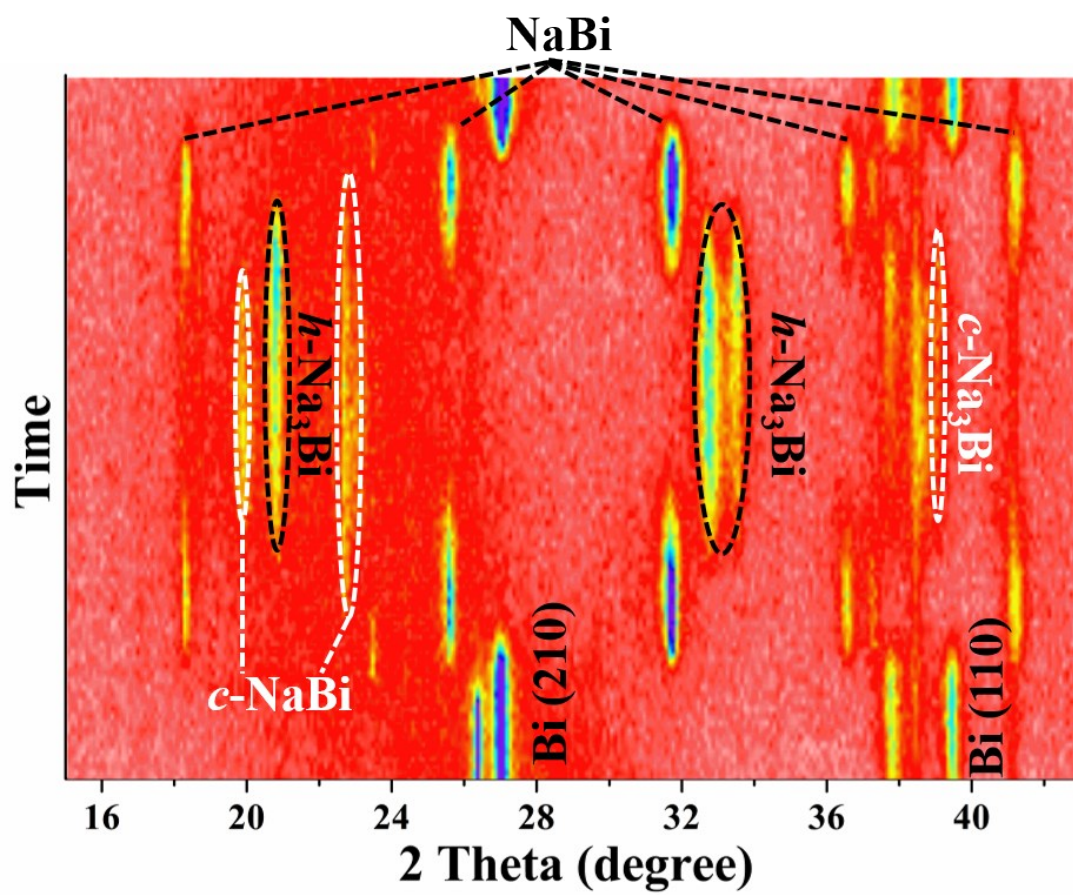


Figure S9. In-situ XRD pattern of Bi-TBAP.

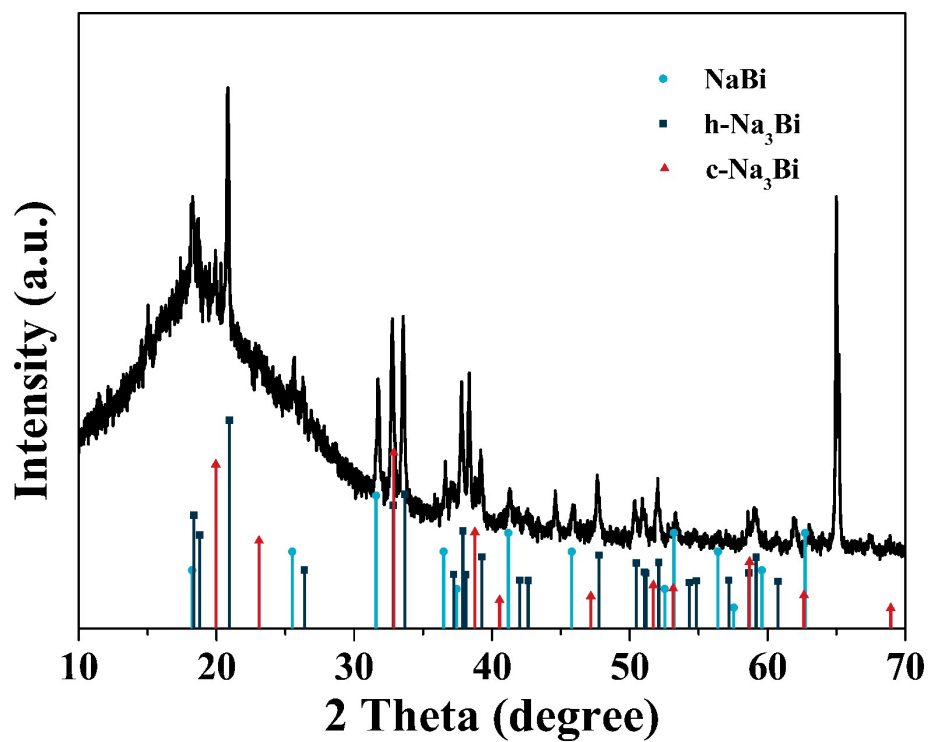


Figure S10. XRD pattern of electrode with Bi-TEAP after several cycles.

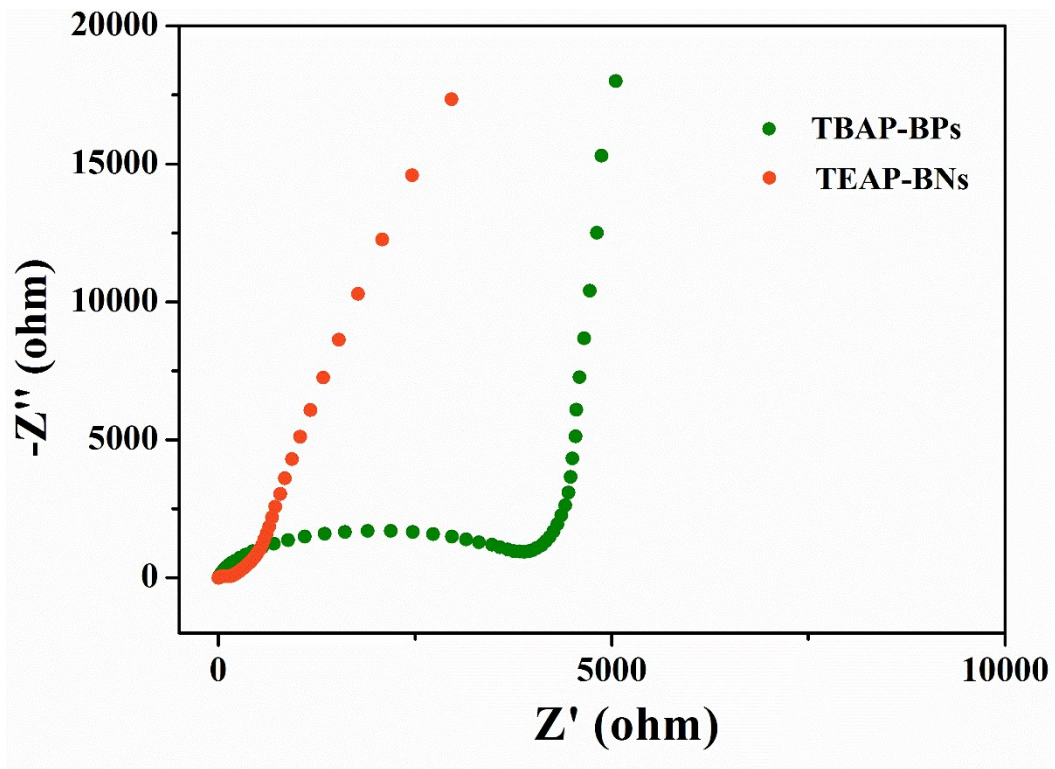


Figure S11. EIS plots of BNs-TEAP and BPs-TBAP

Table S2. SIBs performances comparison for the bismuthine versus other Bi-based materials.

Materials	Current	Cycle (n)	Specific	Rate capacity		Ref.
	density (A g ⁻¹)		capacity (mA h g ⁻¹)	(A g ⁻¹ /mA h g ⁻¹)		
Bi@graphene	0.4	50	≈200	0.8/317	1.28/250	[1]
Bi	0.4	2000	389	0.05/394	2/356	[2]
Bi/Ni	0.2	100	302	0.2/338.4	2/206.4	[3]
Bi-C/CF	0.5	100	630	0.1/550	2.4/110	[4]
Bi _{0.75} Sb _{0.25}	0.5	2000	284	0.25/362	2.5/335	[5]
Bismuthene	1	500	360	0.1/366	2/302	Our work

References

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- [2] C. Wang, L. Wang, F. Li, F. Cheng, J. Chen, *Adv. Mater.* **2017**, *29*.
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