# Poly(5-vinylbenzothiadiazole) for High-Performance Lithium-Ion Batteries

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**ABSTRACT.** Redox-active polymers have recently become promising candidates for next-generation electrode materials in lithium ion batteries. Materials made from small molecules with one or multiple reversible redox states are required to develop high energy-density organic electrodes. Here we focus our attention on 2,1,3-benzothiadiazole (BTZ), a widely employed organic electron acceptor with a suitable redox potential (-1.48 V vs $Ag/Ag^+$ in acetonitrile) and a large theoretical charge-storage capacity (164.5 mAh/g). In this study, we synthesized gram quantities of poly(5-vinylbenzothiadiazole) from BTZ in three synthetic steps, and employed a versatile and scalable radical polymerization protocol to make the final polymer. Lithium-organic hybrid-batteries using this polymer as a cathode displayed a high specific capacity of 140 mAh/g at a charge/discharge potential of 1.70 V vs. $Li/Li^+$. This polymer showed promising performance and high stability, reaching up to 85 % of the theoretical capacity and maintaining 99% coulombic efficiency after 500 cycles at 1C.

**Keywords**: poly(5-vinylbenzothiadiazole), redox-active, polymer, lithium ion battery, high capacity electrode

# INTRODUCTION

The increasing global concerns about environmental pollution and a changing climate associated with the burning of fossil fuels has initiated a strong and rapidly growing demand for storing energy produced from intermittent renewable sources. Using lithium-ion batteries (LIBs) as a means of convenient energy storage has witnessed significant academic and commercial progress over the past two decades,[1] with inorganic transition metal oxides such as $LiCoO_2$ being the most investigated cathode materials in recent years. Recently, organic cathode materials have attracted great interest due to their low cost, light weight, and the possibility of fabricating electrodes entirely of non-toxic and abundant elements.[2-6] The multitude of synthetic variations available for organic materials allows the electrochemical properties and conductivity of organic materials to effectively be changed from the bottom-up to optimize battery performance.

A variety of small molecules and polymers have been investigated as potential electrode materials.[4] The lower molecular weight of small molecules based on light organic elements often results in a higher specific capacity compared to inorganic materials, however their high solubility in the polar electrolyte solutions used in batteries often leads to low cycling stability via electrode dissolution.[7-8] Designing electroactive polymers with highly selective solubility is an attractive strategy to alleviate this problem. Among the molecules that have been incorporated into polymers are carbonyl compounds (i.e., quinones, imides),[9-15] phenothiazine,[16-19] thianthrene,[20] organic radicals,[21-23] dibenzothiophenesulfone,[24] viologen-based materials,[25-26] and flavins.[27] While many of these materials exhibit these materials display good rate performance. They do, however, often have lower theoretical capacities due to the functional groups needed to prevent reactive charged organic species from degrading. These functional groups further complicate the synthesis, making it difficult to scale up production.

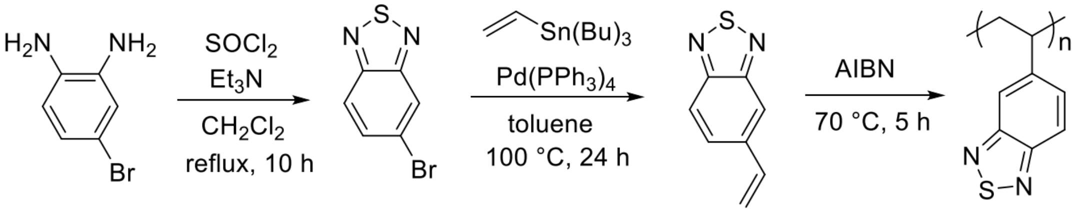
Selecting suitable small molecules with one or multiple reversible redox steps is thus a central focus for the development of high-energy density organic electrodes. 2,1,3-benzothiadiazole (BTZ) is a popular electron acceptor that has been frequently used as an electron-withdrawing moiety for the design of π-conjugated polymers and small molecules in organic solar cells and light-emitting devices.[28-29] BTZ has an equivalent weight of 136 g (mol $e^-$)$^{-1}$ and high solubility in many commonly used organic solvents (e.g. 5.7 M in acetonitrile).[30] These combined characteristics have been utilized to construct high-power nonaqueous organic redox flow batteries by Wei and coworkers,[30] however the high solubility of BTZ in common electrolytes has excluded it from use in traditional rechargeable Li-ion-type batteries to date.[30]

Herein, we have developed poly(5-vinylbenzothiadiazole) as a new electrode material for a hybrid organic/Li-ion battery. This polymer is expected to have several advantages as a battery electrode: (i) incorporating BTZ into a polymer prevents the electrode from dissolving during charging/discharging, (ii) the reversible one-electron reaction of BTZ and low molecular weight provide the resulting polymers with large theoretical charge-storage capacity (164.5 mAh/g), and (iii) its robust redox properties enable high cycle stability. To the best of our knowledge, macromolecules functionalized with redox-active BTZ side groups have been synthesized but not yet investigated as the electro-active material for energy storage.[31] We show that this polymer provides a specific capacity of up to 140 mAh $g^{-1}$ at 1C with a voltage of 1.70 V (v.s. Li/$Li^+$) in a rechargeable Li-ion-type battery.

## RESULTS AND DISCUSSION

The synthetic route toward poly(5-vinylbenzothiadiazole) is presented in Scheme 1. 5-Bromo-2,1,3-benzothiadiazole was synthesized via the reaction of 4-bromobenzene-1,2-diamine with $SOCl_2$ in the presence of $Et_3N$ under reflux for 10 h in a yield of 65%. Subsequent Stille coupling with tri-*n*-butylvinyltin using $Pd(PPh_3)_4$ as the catalyst gave the 5-vinylbenzothiadiazole monomer a yield of 60%. Single crystals of 5-vinylbenzothiadiazole suitable for X-ray crystallography were obtained from slow evaporation of concentrated dichloromethane solutions at room temperature. Its molecular structure in the solid state is depicted in Figure 1, clearly confirming the identity of the synthesized monomer. The crystal data and structure refinement, as well as bond lengths and angles, are summarized in Tables S1 and S2 in the SI.

**Scheme 1.** Synthesis of 5-vinylbenzothiadiazole and its polymer.



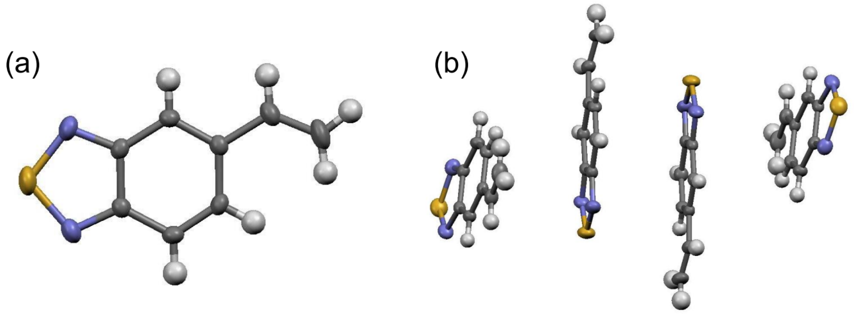


**Figure 1.** (a) Molecular structure of 5-vinylbenzothiadiazole in the solid state (30% probability level) and (b) its intermolecular packing. For crystal data, bond lengths, and angles, see the SI.

Poly(5-vinylbenzothiadiazole) was obtained in a yield of 70% through simple radical polymerization of 5-vinylbenzothiadiazole using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator (typical polymerization conditions: 0.67 M monomer, 0.5 mol% AIBN, in a 1,2-dichloroethane solution). The molecular weight was determined to be $M_n$ = 564,800 (degree of polymerization, DP = 3,490), with a polydispersity of $M_w/M_n$ = 1.7 (Figure S1). After polymerization, three typical $^1$H NMR resonance signals (6.91, 5.98 and 5.50 ppm) from the vinyl group of the monomer disappeared, confirming the successful polymerization. The polymer has a non-polar backbone, imparting good solubility in many common non-polar organic solvents such as THF, allowing the polymer electrode to be easily solution-processed. The non-polar backbone also imparts very poor solubility in polar organic solvents like carbonates, ethers and acetonitrile. This poor solubility in common battery electrolytes makes poly(5-vinylbenzothiadiazole) a suitable electrode material.

While molecular BTZ is highly soluble in polar organic solvents (e.g. 5.7 M in acetonitrile),[30] incorporating BTZ into a polymer makes the material insoluble (less than 0.1 mg/mL) in common battery electrolytes (see the Supporting Information). This structural change prevents capacity fading of the battery device due to electrode dissolution and is indeed an effective strategy for electroactive small molecules. The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA) under an $N_2$ atmosphere. A 5% weight loss appeared at 330 °C, indicative of good thermal stability (Figure S2). The X-ray diffraction spectrum of the drop-cast film from a chloroform solution showed no crystalline peaks, indicating that the polymer is amorphous in the solid state.

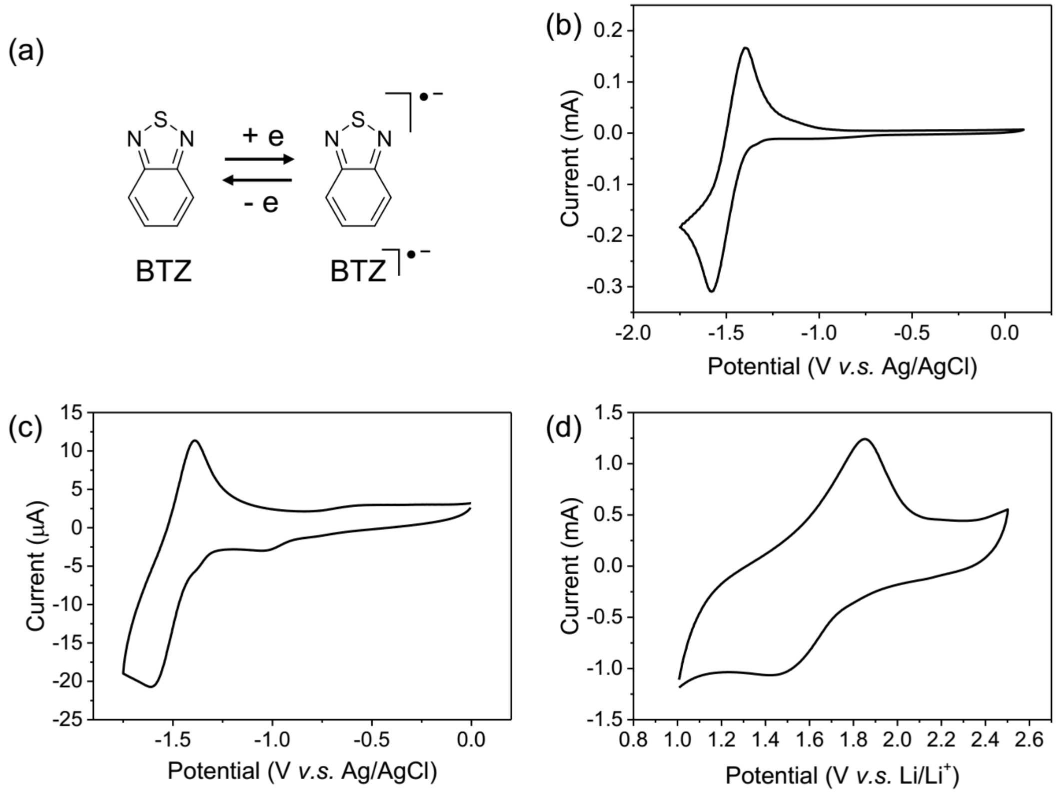


**Figure 2.** (a) Reversible reduction of BTZ, (b) cyclic voltammogram (CV) of BTZ in acetonitrile solution (0.1M $TBAPF_6$ as electrolyte), (c) CV of poly(5-vinylbenzothiadiazole) in 1:1 dichloromethane:tetrahydrofuran solution (0.1M $TBAPF_6$ as electrolyte), and (d) CV of poly(5-vinylbenzothiadiazole)/SWCNT/PVDF (1:1:1) in TEGDME (1.0 M LiTFSI as electrolyte) in a battery configuration.

The electrochemical properties of monomeric BTZ were first examined by cyclic voltammetry (CV) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte (Figure 2b). One reversible reduction was observed at -1.48 V vs. Ag/AgCl, confirming its strong electron accepting ability. This feature is also supported by DFT calculations that confirm the stabilization of the LUMO upon reduction, and a strongly delocalized radical anion across the molecular scaffold (Figure S3). The CV of poly(5-vinylbenzothiadiazole) was conducted in 1:1 THF:DCM using 0.1M $TBAPF_6$ as the electrolyte (Figure 2c). Poly(5-vinylbenzothiadiazole) displays a reversible reduction at around -1.5 V vs. Ag/AgCl, similar to that observed for the monomer, confirming that incorporating BTZ into a polymer does not significantly change its electronic properties. The CVs on the monomer and polymer were conducted in different solvents due to different solubility requirements.

The electrode performance of poly(5-vinylbenzothiadiazole) was evaluated using a half-cell with a Li metal counter electrode. The working electrode consisted of 33.3 wt% poly(5-vinylbenzothiadiazole) as active material, 33.3 wt% single wall carbon nanotube (SWCNT) as the conductive additive, and 33.3 wt% polyvinylidene difluoride (PVDF) as a dielectric and binder. A common electrolyte of 1.0 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) was used as an electrolyte solution. Cyclic voltammograms of the composite electrodes of poly(5-vinylbenzothiadiazole) displayed a quasi-reversible oxidation potential at 1.70 V vs. $Li/Li^+$, as shown in Figure 2. The measured redox potential is in good agreement with that measured in solution.

Figure 3 shows the discharging behavior of the poly(5-vinylbenzothiadiazole) electrode at various C rates (1C, 2C, 5C, 10C, and 20C) in the 1.1–3.45 V range (vs. $Li/Li^+$). "C rate" describes the current density at which the battery is charged and discharged. A rate of 1 C corresponds to a current density that charges or discharges the battery in 1 hour and a rate of 10 C corresponding to 0.1 hour. The electrode with a loading of 1:1:1 polymer:SWCNT:PVDF gave a maximum capacity of 160 mAh/g of active material at a 1C rate on cycle 20 (Figure 3), however this value includes capacitance from the SWCNT additive. We have fabricated a battery using 1:1 PVDF:SWCNT and cycled it at a similar current densities, as well as conducted impedance spectroscopy to determine the relative contribution of the SWCNT to the total capacity. We have determined that around 12% of the total capacity can be attributed to the SWCNT at 1C, making the capacity of the battery 140 mAh/g poly(5-vinylbenzothiadiazole) (see the Supporting Information). The values reported in Figures 3 and 4 represent the total capacity of the battery, and the theoretical maximum capacity of the battery is calculated based on the theoretical contribution of poly(5-vinylbenzothiadiazole). The effect of different C rates (1C, 2C, 5C, 10C and 20C) on the specific capacity has also been examined. Increased charging speeds were found to lead to a decrease of the half-cell capacity from 160 mAh/g (at 1C rate) to 55 mAh/g (at 20C rate). High C rates often result in a decrease in capacity due to the limiting processes such of ion transport and electron conduction, kinetically limiting the usable capacity at higher current densities.[4] This cell still retains 30% of its theoretical capacity at 20C while maintaining a high coulombic efficiency and displaying fast electrode kinetics. In addition, this polymer shows good reversibility for the oxidation and reduction processes during the charging and discharging cycles.

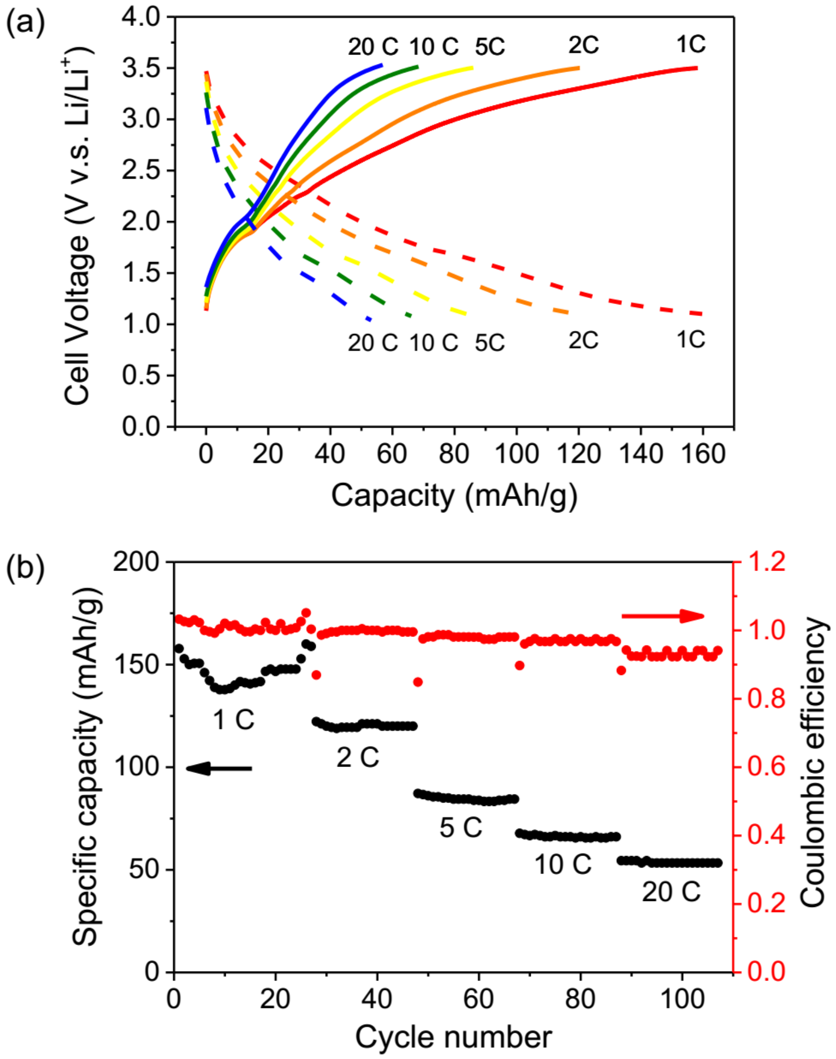


**Figure 3.** (a) Charging/discharging profile of poly(5-vinylbenzothiadiazole)/SWCNT/PVDF composite (1:1:1 ratio) at various C-rates. (b) Capacity and coulombic efficiency as a function of discharge rate for poly(5-vinylbenzothiadiazole). Red dots correspond to coulombic efficiency and black dots correspond to specific capacity (mAh/g).

Our charge/discharge experiments between 1.1 and 3.45 V vs Li/Li+ display only a modest plateau at ~2.0 V. (Figure 3). This behavior is relatively common for organic electrodes and can be attributed in part to relatively poor electron and ion conductivities forcing the redox couple to operate far from equilibrium.[4, 6, 25, 32] It is also worthy to note that our batteries employed poly(5-vinylbenzothiadiazole) as a cathode vs a Li anode; in a fully organic battery it would be used as an n-type material (anode). A similar observation has also been reported for a phosphaviologen-based battery.[25]

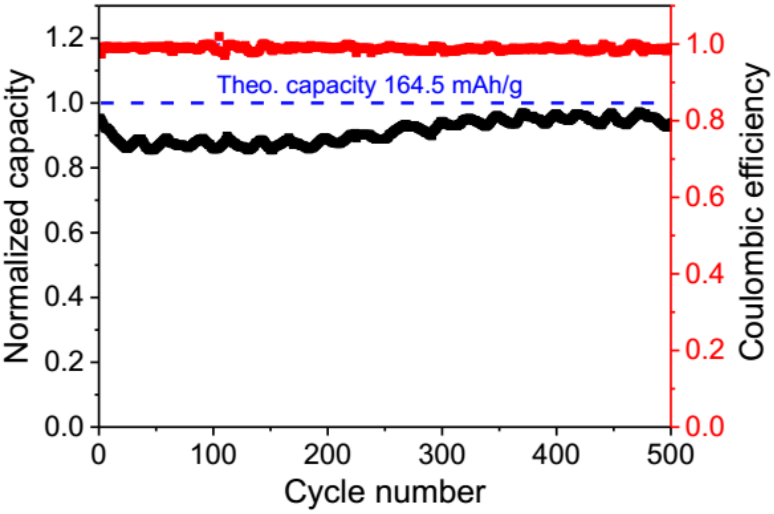


**Figure 4.** Cycle stability for the poly(5-vinylbenzothiadiazole)-based battery at a charging/discharging rate of 1 C in the 1.1–3.45 V voltage range (vs. Li/Li$^+$).

In order to evaluate the cycle stability, the battery was subjected to repeated charge/discharge cycles at 1C in the 1.1–3.45 V (vs. Li/Li$^+$) voltage range. After 500 cycles at 1C, the electrode maintains 90% of its theoretical capacity and charges/discharges with 99% coulombic efficiency (Figure 4). The battery capacity upon cycling initially drops but recovers after the first few cycles; we attribute this behavior to electrode conditioning providing more efficient conductive pathways as the electrode repeatedly swells and expels ions during charging and discharging.

## CONCLUSIONS

In conclusion, we have synthesized and investigated poly(5-vinylbenzothiadiazole) as a cathode-active material in a lithium ion hybrid battery. This polymer is easily accessible in gram quantities via only three simple synthetic steps and shows no detectable solubility in common battery electrolyte solutions. Composite electrodes displayed a promising maximum specific capacity of 140 mAh/g at a charge/discharge potential of 1.70 V vs. Li/Li$^+$. Compared to many other well-known cathode materials in Li-ion battery, such as inorganic $LiCoO_2$ (140 mAh/g) or organic PTMA (111 mAh/g),[20] our polymer provides among the highest specific capacity, making this this current system highly desirable as an organic cathode material for lithium ion battery applications. Overall, this work highlights that benzothiadiazole is a promising building block for incorporation into polymeric systems for energy-storage applications due to its low equivalent weight and suitable reversible redox capability.

## EXPERIMENTAL SECTION

**Materials and Instruments:** PVDF ($M_w$ = 534,000) and LiTFSI (99.5% purity), were purchased from Sigma Aldrich. TBAPF6 was purchased from Sigma Aldrich and recrystallized from EtOH and dried under vacuum before use. SWCNT were purchased from Raymor and used as received. All other chemical reagents were purchased from commercial sources (Aldrich, Alfa Aesar, Strem, Energy Chemical, and Adamas) and used as received, unless otherwise noted. All solvents for the battery fabrication and tests were purchased from Sigma Aldrich, sparged with argon, dried over activated molecular sieves, and stored under argon atmosphere prior to use. All reactions and manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques.

$^{1}$H NMR and $^{13}$C{$^{1}$H} NMR spectra were recorded on 400MHz or 600 MHz BRUKER ARX600 spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. High resolution mass spectra were recorded on a Bruker Daltonics MicrOTOF. IR spectra were obtained on a PE-Frontier instrument. Cyclic voltammetry was performed on an Autolab PGSTAT204 instrument. Polydispersity indices (PDI = $M_w/M_n$) of all the polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek TM Triple-Detector Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, inline degasser, column oven (35 °C), and RI, viscometry, and light scattering detectors. A flow rate of 1.0 mL/min was used with THF as the eluent. Samples were dissolved in the eluent (1 mg/mL) and filtered (PTFE membrane with 0.45 $\mu$m pore size) before analysis. Calibration of the detectors was performed using polystyrene standards (Viscotek).

**Synthesis of 5-bromo-2,1,3-benzothiadiazole:** Thionyl dichloride (6.53 g, 54.9 mmol) was added dropwise in 30 min to a mixture of 4-bromobenzene-1,2-diamine (5.10 g, 27.3 mmol) and triethylamine (11.22 g, 111.0 mmol) in 150 ml dichloromethane at 0 °C. The resulting mixture was then heated to reflux for 10 h. After being cooled to room temperature, the reaction mixture was washed with water and then brine, and was then dried over anhydrous $MgSO_4$. Solvent evaporation from the extract gave a crude product, which was purified by chromatography using petroleum to yield 3.80 g (65 %) of the desired product as white solid. $^{1}$H NMR (600 MHz, $CDCl_3$): $\delta$ (ppm) = 8.22 (s, 1H, Ar*H*), 7.88 (d, 1H, $J$ = 9.0 Hz, Ar*H*), 7.67 (d, 1H, $J$ = 9.0 Hz, Ar*H*). $^{13}$C{$^{1}$H} NMR (150 MHz, $CDCl_3$): $\delta$ (ppm) = 155.3, 153.3, 133.2, 124.5, 123.8, 122.2. HRMS (ESI-TOF) $m/z$ = 214.9271 $[M+H]^+$ (calcd. 214.9279).

**Synthesis of 5-vinylbenzothiadiazole**: 5-bromo-2,1,3-benzothiadiazole (860 mg, 4 mmol), 2,6-di-*t*-butyl-*p*-cresol (1.02 mg, 4.6 $\mu$mol), and tetrakis(triphenyl-phosphine)palladium(0) (139 mg, 0.12 mmol) were transferred to 2-necked round bottom flask equipped with condenser under $N_2$. Anhydrous toluene (20 mL) and tri-*n*-butylvinyltin (1.90 g, 6 mmol) were then added via a syringe to the mixture under nitrogen. The resulting mixture was stirred at 100 °C for 24 h. After cooling to room temperature, all the volatiles were removed under vacuum. The residue was purified using silica gel column chromatography using petroleum ether as an eluent, to yield 5-vinylbenzothiadiazole as a white solid (385 mg, 60%). Single crystals of the 5-vinylbenzothiadiazole monomer suitable for X-ray crystallography were obtained from slow evaporation of concentrated dichloromethane solutions at room temperature. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) = 7.97 (d, 1H, $J$ = 9.2 Hz, Ar*H*), 7.90 (s, 1H, Ar*H*), 7.81 (d, 1H, $J$ = 9.2 Hz, Ar*H*), 6.91 (dd, 1H, $J$ = 17.6 and 10.8 Hz, vinyl *H*), 5.98 (d, 1H, $J$ = 17.6 Hz, vinyl *H*), 5.50 (d, 1H, $J$ = 10.8 Hz, vinyl *H*). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) = 155.4, 154.6, 138.8, 135.8, 127.5, 121.3, 119.0, 117.0. HRMS (ESI-TOF) *m/z* = 163.0325 $[M+H]^+$ (calcd. 163.0330).

**Synthesis of poly (5-vinylbenzothiadiazole)**: 5-Vinylbenzothiadiazole (1.62 g, 10 mmol) and AIBN (8.2 mg, 0.05 mmol) were dissolved in anhydrous 1,2-dichloroethane (15 mL) (boiling point: 83.5 °C) under nitrogen. The solution was then heated to 70 °C for 16 h. Then, the reaction mixture was poured into methanol and a white precipitate formed. The precipitate was washed with methanol, dissolved in 1,2-dichloroethane, and re-precipitated with methanol, to yield a white powder (1.05 g, 70 %). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ (ppm) = 8.20-6.20 (br, Ar*H*), 2.50-0.70 (br, ethylenyl *H*). $^{13}$C{$^1$H} NMR (150 MHz, $CDCl_3$): $\delta$ (ppm) = 154.3, 153.3, 144.7, 128.8, 121.2, 119.4, 41.0, 29.7. Gel permeation chromatography (THF eluent, polystyrene standard): $M_n$ = 564,800, $M_w/M_n$ = 1.7.

**Cyclic voltammetry:** Cyclic voltammetry was conducted on a 10mg/mL poly(5-vinylbenzothiadiazole) solution in dry, degassed 1:1 DCM:THF containing 0.1M $TBAPF_6$. A typical three-electrode cell was used having a Pt wire as a counter electrode, glassy carbon as a working electrode, and Ag/AgCl as a reference electrode.

**Electrode Preparation:** poly(5-vinylbenzothiadiazole) and SWCNT are combined at a 1:1 ratio and dissolved in NMP at 20 mg/mL. The solution is sonicated for 15 minutes and stirred at 90 °C for 1 hour. A separate solution of 20 mg/mL of PVDF in NMP is prepared and stirred at 90 °C until it dissolves. Enough NMP/PVDF solution is added to the solution of NMP/poly(5-vinylbenzothiadiazole)/SWCNT to create a 1:1:1 mixture of the components and this solution is sonicated for 15 minutes then stirred at 90 °C for 1 hour. 0.1 mL of the slurry is evenly spread over the electrode (18 mm diameter carbon coated copper) and dried at 90 °C. The electrode is then dried under vacuum at 90 °C for 72 hours before being used in a battery. The total amount of material per electrode is around 2 mg giving an areal density of around 1 mg/cm$^2$.

**Battery Testing:** The battery is assembled using an EL-cell ECC-ref reusable test cell in a coin cell geometry using a lithium reference and 1.0 M LiTFSI in TEGDME electrolyte. A lithium foil of diameter 18 mm was used as the anode, an 18 mm diameter glass fiber separator (EL-cell) was used to prevent short circuiting, and carbon coated copper (EL-cell) was used as the cathodic current collector. Li coins were cut using an ECC Li-punch press and C/Cu coins were cut using an EL-cut punch from EL-cell. A stack consisting of lithium foil : glass fiber impregnated with 0.35 mL electrolyte : electrode was sealed in the battery cell inside of a glove box with an argon atmosphere before being used in cyclic voltammetry and battery cycling experiments. Current densities for different C-rates were calculated assuming poly(5-vinylbenzothiadiazole) has a specific capacity of 164.5 mAh/g. The electrodes were weighed before and after depositing the 1:1:1 Poly(5-vinylbenzothiadiazole : SWCNT : PVDF composite, and the mass of poly(5-

vinylbenzothiadiazole is calculated assuming it is 33% of the total mass of deposited electrode material.

## ASSOCIATED CONTENT

**Supporting Information**. The crystal data and structure refinement, as well as bond lengths and angles of 5-vinylbenzothiadiazole, TGA and GPC of poly(5-vinylbenzothiadiazole), NMR spectra, and theoretical calculation of BTZ.

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### Notes

The authors declare no competing financial interest.

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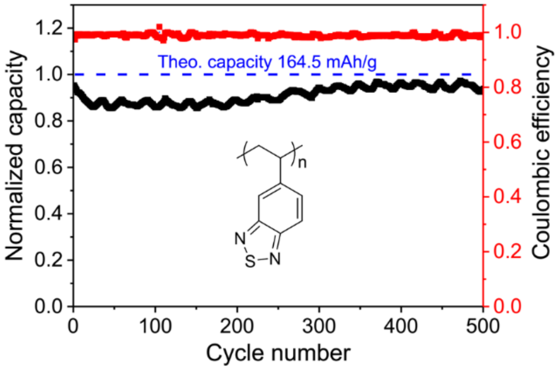
## TOC GRAPHIC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Normalized capacity
Coulombic efficiency
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500
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0.6
0.8
1.0
1.2
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