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s-Tetrazines as a new electrode-active material for secondary batteries

Dong Joo Min,^[a] Fabien Miomandre,^[b] Pierre Audebert,^[b] Ji Eon Kwon,*^[a] and Soo Young Park*^[a]

Abstract: Due to the limitations of the conventional metal oxidebased electrodes, studies on organic redox-active materials as alternative electrodes for secondary batteries are emerging. Nonetheless, the reported organic electrode materials are still limited to a few kinds of organic redox groups. Developing new redox-active groups for high-performance electrode materials is therefore indispensable. Here, we evaluate s-tetrazine derivatives as a new electrode material in Li-ion batteries for the first time and study their charge/discharge mechanisms by ex-situ XPS measurements. The porous carbon CMK-3 is introduced to encapsulate the s-tetrazines, which allows 100% utilization of the theoretical capacity and stable cycle performance of the s-tetrazines by preventing dissolution of the molecules into the electrolytes. We believe that this new class of redox-active group can pave the way for the next-generation energy storage system.

Introduction

Since the first commercialization by Sony in 1991, Li-ion battery (LIB) based on transition metal oxides has achieved great success in the market and has become indispensable in our daily lives.^[1,2] However, with emerging demand for sustainable and green battery, development of the conventional inorganic electrode materials faces their limits.^[3,4] As a promising alternative, organic electrode materials are drawing much attention due to their potential advantages of low-cost, natural environmental friendliness, and structural abundance. diversity.^[5,6] Indeed, the last decade has witnessed great advances in organic electrode materials. But, most of the research so far has focused on only a few kinds of redox-active groups, which are limited to conjugated carbonyls,^[7-10] organosulfurs,^[11,12] conducting polymers^[13-16] and nitroxide radicals.^[17,18] Although those organic electrodes showed great potential in LIBs as well as in some earth-abundant metal ion batteries (e.g., sodium, magnesium, zinc, etc.),[19-21] critical obstacles still exist for their practical use such as low rate performance and fast capacity fading.[22-25] In this regard, the search for a new redox-active group to achieve highperformance organic electrode is highly desired.

1,2,4,5-Tetrazine, also known as s-tetrazine, is the most electron

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deficient six-membered aromatic ring among the C-N heterocycle system that can stably exist at room temperature.^[26] Because it has a high electron affinity and intriguing $n-\pi^*$ transition character with strong fluorescence, various s-tetrazine derivatives have been extensively studied as electron poor dienes in inverse demand cycloaddition reactions,[27] fluorophores in chemosensors,[28] and active materials in nonlinear optics (NLO),^[29] in transistors^[30] and in solar cells.^[31] In particular, it is well known that the s-tetrazine derivatives can undergo reversible reduction by accepting one electron to form very stable anion radical due to the strong electron deficient character (Figure 1a).^[32] Based on the redox-activity, Audebert Kim groups demonstrated the construction and of electrofluorochromic window devices using polymer electrolyte films containing s-tetrazine derivatives.[33] Despite the promising electrochemical properties, to the best of our knowledge, the potential applicability of s-tetrazines to electrode active materials in secondary batteries has not been explored to date.

In this work, we report on a novel application of s-tetrazines as electrode-active materials in a secondary battery for the first time. We prepared a series of s-tetrazine derivatives bearing various substituents including phenyl, alkoxy, and chlorine (Figure 1b). It is expected that the redox potential of the s-tetrazines is finely tuned according to the electron donating or withdrawing capability of the substituents.^[34]

Results and Discussion

The synthesis of 3,6-dichloro-1,2,4,5-tetrazine (DCT) was conducted through 5 steps, of which the total yield was 44% (see experimental details and Figure S1 in the supporting information).^[35] 3,6-Dimethoxy-1,2,4,5-tetrazine (DMT) and 3-chloro-6-ethoxy-1,2,4,5-tetrazine (CET) were then synthesized by nucleophilic substitution of DCT.^[26,28,33] The 3,6-diphenyl-1,2,4,5-tetrazine (DPT) was purchased from a commercial supplier.

Density functional theory (DFT) calculation revealed that the lowest unoccupied molecular orbital (LUMO) energy level of the s-tetrazines significantly varies according to the substituents (Figure 1d and Figure S3). DPT bearing two electron donating phenyl groups has the highest LUMO energy (-2.96 eV), whereas the LUMO energy of DCT (-4.07 eV) bearing two electron-withdrawing Cl groups is the most stabilized among the series. The LUMO of a molecule is the energy state where the electron is inserted in the reduction process; therefore, we anticipated that the redox potential of the s-tetrazine series would be tuned accordingly.

To investigate the practical redox potential of the s-tetrazines, cyclic voltammetry (CV) was performed in acetonitrile solutions with 0.01 M AgNO₃/Ag as a reference electrode. All s-tetrazines showed a reversible one-electron redox reaction, and the redox potentials ($E_{1/2}$) were -0.54, -0.85, -1.11, and -1.18 V vs. Ag⁺/Ag for DCT, CET, DMT, and DPT, respectively, at a scan

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Figure 1. (a) Redox reaction of the s-tetrazines. (b) Molecular structures of the s-tetrazine derivatives used in this study. (c) Cyclic voltammetry (CV) of the s-tetrazines in 0.1 M [NBu₂][PF₆] acetonitrile (CH₃CN) solution. Scan rate (*v*) was 50 mV s⁻¹ with a 3mm glassy carbon working electrode. The concentration of tetrazine derivatives was 5 x 10⁻³ M in CH₃CN except for DPT (3 x 10⁻³ M) which has lower solubility in CH₃CN than the others. (d) The plot of calculated LUMO level by the DFT method vs. experimental redox potential measured by CV.

rate of 50 mV s⁻¹ (Figure 1c). As expected, the s-tetrazines possessing electron withdrawing groups exhibited higher redox potentials than ones having electron donating groups. It should be noted that the measured redox potentials well correlate with the LUMO energy level trend calculated by the DFT methods (Figure 1d).^[36,37]

Encouraged by the redox reversibility of the s-tetrazines in the solution, we fabricated electrodes composed of the s-tetrazines as an active material, carbon black (Timcal Super P) as a conductive additive, and PVDF as a binder. The electrochemical properties of the electrodes were tested in CR2032 coin cells using lithium metal foil as an anode. We first chose 1 M LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) as an electrolyte (referred to as 1ED) because it is one of the most conventional electrolytes for LIBs. In the galvanostatic test at 0.1 C rate (1 C = 114 mA g⁻¹ for DPT), DPT showed a set of plateaus at 2.2 and 2.3 V vs. Li+/Li during discharge and charge, respectively, well corresponding with the solution CV results. The discharge specific capacity of the DPT electrode was 172 mAh g⁻¹ at the first cycle, which is higher than its theoretical capacity most likely due to a formation of solid electrolyte interfaces (SEI).^[38] However, a rapid decrease of the specific capacity was observed during subsequent cycles due to its rather high solubility in the 1ED electrolyte (Figure S4a, b).

To improve the cycle stability, we changed the electrolyte to 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1:1 (v/v) mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (referred to as 1DD). Because the ether-based solvents (*i.e.*, DOL and DME) have lower polarity than the carbonate-based ones (*i.e.*, EC and DMC), organic materials typically show lower solubility in the former. Recently, much improved cycle

performance using the ether-based electrolytes have been reported in several papers.^[39,40] In 1DD electrolyte, DPT showed cycle retention with sharper plateaus better in the discharge/charge profiles (Figure S4 in SI). In particular, by increasing the concentration of LiTFSI salt to 2 M in the electrolyte (referred to as 2DD), the cycle stability of DPT could be more improved (Figure 2a and Figure S4 in SI). It is most likely that the dissolution of the s-tetrazines was more effectively prevented in the electrolyte with higher salt concentration because of the common ion effect.^[41] In 2DD, the DPT electrode delivered a discharge capacity of 72 mAh g⁻¹ at the first cycle, but 58% of the initial capacity could remain after the 20th cycle at 0.1 C (Figure 2a, c). The differential capacity plot of DPT clearly displays discharge and charge voltages at 2.24 and 2.31 V, respectively (Figure S6a).

In contrast, DCT bearing two electron withdrawing chlorine atoms exhibited a broad discharge/charge profiles with an initial discharge capacity of 96 mAh g⁻¹ (54% of its theoretical capacity) at 0.1 C (1 C = 177 mA g⁻¹ for DCT) in the 2DD electrolyte (Figure 2b, d). Interestingly, the differential capacity plot of DCT electrode shows two discharge/charge peaks at 2.66/2.97 and 2.33/2.77 V (Figure S6b in SI). In the solution CV, DCT exhibited only one redox couple but at much higher voltage region than DPT (*vide supra*, Figure 1c). It is therefore reasonable to infer that the DCT electrode underwent an unwanted side reaction in the coin cell due to the CI substituents. It will be discussed by the ex-situ XPS studies below. The capacity retention of DCT electrode after 20 cycles was 52% which is similar to that of DPT.

On the other hand, CET and DMT showed only a negligible specific capacity in the coin cells (Figure S7). This is an artifact attributed to the high volatility of the two small s-tetrazine molecules. Since the melting points (T_m) of CET (58 °C) and DMT (57 °C) are significantly lower than those of DPT (201 °C) and DCT (145 °C) (Figure S8), it is postulated that most of the CET and DMT molecules are easily removed from the



Figure 2. Specific capacities with the corresponding coulombic efficiency (blue triangles) of (a) DPT and (b) DCT along the charge (black squares) and discharge (red circles) cycles at 0.1 C rate in the 2DD electrolyte. The charge/discharge profiles of (c) DPT and (d) DCT at the first (black squares) and 20th (red triangles) cycle, respectively at 0.1 C rate in the 2DD electrolyte.

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Figure 3. Ex-situ XPS spectra of the DPT electrodes at different states of charge: (a) Li 1s, (b) N 1s, and (c) C 1s region. Ex-situ XPS spectra of the DCT electrodes at different states of charge: (d) Li 1s, (e) N 1s, and (f) Cl 2p region. The black, red, and blue lines indicate pristine, discharged, and recharged state, respectively.

electrodes by sublimation during the electrode fabrication process particularly in the vacuum oven. The higher T_m of DPT and DCT than DMT and CET are most likely attributed to the increased intermolecular interactions through π - π and halogen-halogen interactions, which can be induced by their diphenyl and dichloro substituents, respectively.

To elucidate the electrochemical redox mechanism of DPT and DCT, the discharged/recharged electrodes were examined by ex-situ X-ray photoelectron spectroscopy (XPS). In the Li 1s spectra of DPT (**Figure 3a**), a lithium peak at 55.6 eV clearly evolved upon discharge and then completely disappeared by recharge, indicating a reversible lithium ion binding during

reduction/reoxidation process. Simultaneously, a reversible peak shift was observed in the N 1s spectra (Figure 3b). The pristine electrode of DPT showed only a single N 1s peak at 400.28 eV because the nitrogen atoms of the s-tetrazine ring (–N=) have identical bonding nature due to the resonance structure. Upon discharge, the peak slightly shifted to 399.70 eV; subsequently, it was restored to its original position by the recharge process. It should be noted that the shift of N 1s peak is rather small compared to that of other organic molecules bearing an N atom as a redox-active site. For example, in the case of pteridine derivatives,^[42] when the molecules are reduced, and the nitrogen atom of the pteridine gets one electron with a Li-ion, the binding

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Figure 4. FE-SEM images of (a) DPT, (b) CMK-3, (c) composite A, (d) composite B, and (e) composite C. The scale bar is 2 µm.

energy of N 1s is decreased by more than 1 eV. In sharp contrast, when DPT was reduced by one electron, the binding energy of N 1s of DPT is decreased by ~ 0.6 eV without the appearance of any additional peak. It implies that the nitrogen atoms in the reduced DPT undergo less shielding effect because the all four nitrogen atoms in the s-tetrazine ring effectively share the added electron through the resonance structure.^[43]

In the case of C 1s spectrum, the peaks of the pristine DPT electrode could be deconvoluted into four main contributions including a C–(C, H) sp2 peak of aromatic carbons and conductive carbons (284.5 eV), –CH2–, –CF2– peaks of PVDF (285.7 eV and 290.5 eV, respectively),^[44] and a peak (–C–C=N–) of the s-tetrazine ring carbon (286.76 eV) (Figure 3c). After being discharged, no salient spectral change was observed except a shift of the s-tetrazine ring carbon peak to the lower energy side. But, upon recharge, the peak reversibly shifted back to its original position. Based on the above XPS results, it is reasonable to infer that all atoms of the tetrazine core ring of DPT share the added electron with a Li cation by the discharge and reversibly release them by the recharge process (see Figure S13 in the supporting information for the plausible reaction scheme).

Similarly, reversible spectral changes were observed in the N 1s spectra of the DCT electrode during discharge/charge process (Figure 3e). But, it seems that a very weak signal still remained after recharge in the Li 1s spectrum of DCT (Figure 3d). In addition, Cl 2p and C 1s spectra of DCT obviously showed irreversible aspects. In the pristine DCT electrode, two Cl 2p peaks were observed due to the spin-orbit splitting (Figure 3f).^[45] Upon discharge, new two peaks evolved at around 199 and 198 eV, corresponding to binding between Li and Cl. After recharge, it was observed that the peaks of Li-Cl were reduced, but a considerable intensity of the peaks remained, implying irreversibility of the redox reaction.

In the C 1s spectrum of discharged DCT, the carbon peak (–C– C=N–) of the s-tetrazine ring shifted to lower binding energy due to reduction. But, in sharp contrast to the DPT case, a new peak at around 288 eV simultaneously appeared upon discharge, which maintained its intensity even after recharge process (Figure S9). Moreover, the carbon peak of s-tetrazine ring did not shift back to its original position. Taking into account the XPS results and the dQ/dV plots, it is deduced that an irreversible redox reaction occurred in addition to the reversible redox of s-tetrazine ring during discharge/charge in the DCT electrode. The Li-Cl binding must be involved in the reactions and most likely triggered a further irreversible reaction such as cleavage of the Cl from carbon atoms in the s-tetrazine ring.

Through the ex-situ XPS studies, we have found that the DPT electrode can store/release a Li⁺ ion reversibly. However, rather low specific capacity compared to its theoretical one and severe capacity fading are limiting factors toward practical application. To improve the capacity utilization and retention of DPT, we fabricated composite materials by infiltrating the DPT molecules into the nano-size pores of porous carbon CMK-3. This method was originally developed to prevent the dissolution of polysulfide in Li-S battery^[46-48] and recently has been successfully implemented in Li-Organic batteries by several groups including us.^[49,50]

To find the optimum mixing ratio, three composite materials were prepared by mixing DPT and CMK-3 in weight ratios of 2:1 (composite A), 1:1 (composite B), and 1:2 (composite C), respectively. In FT-IR spectra, the C-N stretching peak of the stetrazine ring at around 1390 cm⁻¹ was clearly observed from the composites A and B (Figure S10a). Similarly, in powder X-ray diffraction (PXRD) data, the two composites exhibited strong diffraction patterns (Figure S10b-d). In contrast, it was observed that the FT-IR peaks and the diffraction patterns were much reduced in the composite C, implying that most of the DPT molecules are well encapsulated by the CMK-3 nanostructures. In the FE-SEM images, it is clearly seen that there is an excess amount of DPT molecules aggregated outside of the CMK-3 pores in the composite A and B. On the other hand, DPT molecules existed almost only inside the CMK-3 pores in the composite C (Figure 4). The dissolution of the three composite electrodes were monitored by immersing them in the 2DD electrolyte solutions, respectively (see Figure S11 in the supporting information). It should be noted that the solution containing the composite C electrode showed a very faint color change even after 12 h, while the pristine DPT and the other two





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composite electrodes turned the solutions into clear pink color. It indicates that the DPT molecules were well encapsulated inside the pores of CMK-3 and thus their dissolution was effectively prevented in the composite C. In contrast, in the case of the other two composites (i.e., composite A and B), the excessive DPT molecules outside the CMK-3 pores (see Figure 4c and d) would dissolve into the solutions to make their color pink.

Figure 5a exhibits the galvanostatic discharge/charge profiles of the composites at a 0.1 C rate at the first cycle (1 C = 114 mA g ¹ for the composites). The composites showed rather broad discharge/charge plateaus compared to the bare DPT electrode. But, it is noteworthy that not only the capacity utilization at the first cycle but also the retention at subsequent cycles were significantly improved in the composites. In particular, the composite C delivered an initial capacity of 116 mAh g⁻¹, which is virtually the same as its theoretical capacity, and maintained 80% of its initial capacity even after 20 cycles at 0.1 C rate. Furthermore, the composite **C** electrode showed much improved cycle stability during 300 charge/discharge cycles at 1 C rate. After 300 cycles, it still could deliver a discharge capacity of 99 mAh g⁻¹, which corresponds to 82.5% of the discharge capacity at the second cycle. This indicates that the DPT molecules were well infiltrated into the CMK-3 nanostructures to prevent its dissolution and also to facilitate utilization.

Conclusions

In summary, a series of s-tetrazine derivatives were prepared, and their electrochemical properties were evaluated as new organic electrode materials for rechargeable Li-ion batteries for the first time. Ex-situ XPS and dQ/dV analyses revealed that the DPT electrode could reversibly store and release a Li-ion through a redox reaction of the s-tetrazine ring at around 2.3 V vs. Li*/Li. In contrast, the CI atoms substituted in the s-tetrazine ring of DCT caused irreversible redox reactions with Li-ions. To suppress dissolution of DPT into the electrolyte, we fabricated composite materials by infiltrating DPT molecules into the nanoporous carbon CMK-3. The DPT molecules were well confined inside CMK-3 when the mixing ratio of DPT:CMK-3 was 1:2 in weight. The composite electrode showed much improved cycle stability during 300 charge/discharge cycles at 1 C rate. Although the redox potential of the DPT electrode lies in the middle between the typical anodes and cathodes in Li-ion cell, we would like to emphasize that its redox activity is definitely stable and reversible. Therefore, we can expect that DPT is able to be used as anode materials for other metal ion batteries possessing higher standard reduction potential than Li (-3.04 V vs. SHE) such as Na (-2.71 V vs. SHE) and Mg (-2.37 V vs. SHE). Furthermore, based on their easy derivatization and tunability of redox potential, we also believe that the s-tetrazine moiety has great potential as a new redox-active group for electrode materials not only in the solid electrode type batteries but also in organic redox flow batteries.

Experimental Section

Materials and General Methods: Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI), 1,3-dioxolane (DOL), and dimethoxyethane (DME) were purchased from Sigma-Aldrich. 3,6-diphenyl-1,2,4,5-tetrazine (DPT) and CMK-3 were purchased from TCI and ACS material, respectively. 3,6-dichloro-1,2,4,5tetrazine (DCT) and 3,6-dimethoxy-1,2,4,5-tetrazine (DMT) were prepared according to the reported procedures^[26, 35] and the synthetic details are described in the following synthesis section. Reactions were monitored using thin layer chromatography (TLC) with commercial TLC plates (silica gel 60 F254, Merck Co.). Silica gel column chromatography was performed with silica gel 60 (particle size 0.063-0.200 mm, Merck Co.). ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 300 spectrometer. The powder XRD data were collected using a Bruker D8 Advance with a Davinci diffractometer equipped with Cu Ka (λ = 1.5418 Å) radiation. Field emission scanning electron microscopy (FE-SEM) images were acquired using a ZEISS MERLIN Compact with a 2 kV accelerating voltage. ATR/FT-IR was performed on a Thermoscientific Nicolet 6700 spectrometer.

Synthesis of Triaminoguanidine hydrochloride (1): To a slurry of guanidine hydrochloride (25.00 g, 0.26 mol) in 1,4-dioxane (130 mL) was added hydrazine monohydrate (52.40 g, 1.05 mol) with stirring. The mixture was heated under reflux for 2 h. After the mixture cooled down to room temperature, the product was washed with 1,4-dioxane, and dried to give 32.79 g (89%) of triaminoguanidine monohydrochloride. ¹³C NMR (75 MHz, D₂O, δ): 159.5.

Synthesis of 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2-dihydro-1,2,4,5tetrazine (**2**): To a solution of **1** (32.00 g, 0.23 mol) in water (225 mL) was added acetylacetone (49 mL, 0.48 mol) dropwise with stirring at 25 °C. After the mixture had stirred at 25 °C for 0.5 h and it was heated overnight at 70 °C. The product was washed with water and dried to yield 24.91 g of the product (80%). ¹H NMR (300 MHz, CDCl₃, δ): 2.22 (s, 6H), 2.49 (s, 6H), 5.96 (s, 2H), 8.05 (s, 2H).

Synthesis of 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine (3): In a two neck round bottom flask, a solution of sodium nitrite (18.62 g, 0.27 mol) in 390 mL of water was prepared, and 35 mL of dichloromethane was added. 2 (24.50 g, 0.09 mol) was introduced to the flask at 0 °C. Acetic acid (13 mL, 0.22 mol) was added dropwise to the solution. After 12 h, the organic layer was extracted with dichloromethane. The organic layer was washed by 5% aqueous solution of potassium carbonate, dried with MgSO₄ and filtered. The crude product was obtained by evaporation of the solvent under reduced pressure. The dark red solid obtained was washed several times with diethyl ether to give 23.155 g (95%) of 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine. ¹H NMR (300 MHz, CDCl₃, δ): 2.40 (s, 6H), 2.72 (s, 6H), 6.20 (s, 2H).

Synthesis of 3,6-dihydrazineyl-1,2,4,5-tetrazine (4): To a slurry of 3 (20 g, 0.07 mol) in acetonitrile (125 mL) was added hydrazine monohydrate (8 mL, 0.16 mol) dropwise at room temperature. After the addition, the mixture was refluxed for 1 h. The mixture was the cooled down to room temperature, filtered, and washed with acetonitrile to afford 3,6-dihydrazineyl-1,2,4,5-tetrazine in quantitative yield.

Synthesis of 3,6-dichloro-1,2,4,5-tetrazine (DCT): To a slurry of **4** (10 g, 0.07 mol) in acetonitrile (280 mL) at 0 °C was added dropwise over 30 min a solution of trichloroisocyanuric acid (34.34 g, 0.15 mol) in acetonitrile (200 mL). After the addition was finished, the reaction vessel was stirred at room temperature for 20 min. The white insoluble precipitate was removed by filtration and the volatiles removed in vacuo to give crude product which was passed through a short column chromatography (SiO2, 1:1 (v/v) mixture of dichloromethane/petroleum

ether) to afford 7.16 g (67%) of pure product as an orange powder; ^{13}C NMR (125 MHz, CDCl₃, $\delta):$ 168.3.

Synthesis of 3,6-dimethoxy-1,2,4,5-tetrazine (DMT): DCT (0.50 g, 3.31 mmol) was dissolved in 8 mL of anhydrous methanol. At 25 °C, Na₂CO₃ (1.75 g, 16.55 mmol) was added dropwise to the solution, and MgSO₄ was added for solvent dryness. The reaction mixture was stirred at 65 °C. After removal of the solvent, the crude product was purified by silica gel column chromatography using 1:1 (v/v) dichloromethane/hexane eluent mixture to give 145 mg of red solid (30.8%). ¹H NMR (300 MHz, CDCI3, δ) 4.26 (s, 6H), ¹³C NMR (125 MHz, CDCI3, δ) 166.58 (C of the tetrazine ring), 56.87 (C of the methoxy).

Synthesis of 3-chloro-6-ethoxy-1,2,4,5-tetrazine (CET). DCT (0.50 g, 3.31 mmol) was dissolved in 15 mL of anhydrous dichloromethane, and added successively 0.2 mL (1.2 eq.) ethanol and 0.4 g (1 eq) collidine, and stirred about 1 h at room temperature. CET was purified by chromatography (Pet. Ether 3/Dichloromethane 1) and 0.46g of powder was recovered (81%). ¹H NMR (300 MHz, CDCI3, δ) 4.74 (q, 2H), 1.59 (t, 3H), ¹³C NMR (125 MHz, CDCI3, δ) 166.75, 164.39, 67.17, 14.34.

Ex-situ XPS: The electrodes were prepared at different states of charge (as-prepared, discharged to 2 V, and recharged to 2.7 V (DPT) or 3.5 V (DCT)), respectively. To prevent exposure to air, all samples were moved to Ar-filled glove box before opening the coin cells. After disassembling the coin cells, the electrodes were washed several times with DOL and DME to remove the residual electrolytes. Subsequently, the residual solvents were removed from the electrode in a vacuum chamber. Then, the electrodes were sealed in Ar-filled vials. XPS measurements were conducted with a ULVAC-PHI 5000 VersaProbe equipped with a microfocus monochromated Al K α (1486.6 eV) X-ray. All samples were analyzed at an electron take-off angle of 45 degree, measured from the surface plane. Binding energies were referenced to the C–C bond of the C 1s region at 284.5 eV.

Theoretical Calculation: All density functional theory (DFT) calculations were carried out in the gas phase using the Gaussian 09 quantumchemical package. The geometry optimizations were performed using Becke-Lee-Yang-Parr (B3LYP) functionals and the 6-31G+(d,p) basis set. Vibrational frequency calculations were performed for the obtained structures at the same level to confirm the stable minima.

Electrochemical Measurement: Cyclic voltammetry (CV) was performed on a Princeton Applied Research Model 273a using a three-electrode beaker cell with 0.01 M AgNO₃/Ag as a reference electrode, a glassy carbon disc (diameter = 3 mm) as a working electrode, and a platinum wire as a counter electrode, respectively. The redox potential of reference electrode was calibrated using ferrocenium/ferrocene (Fc⁺/Fc) as an internal standard. The tetrazine solutions were made to be 5 × 10⁻³ M in CH₃CN except for DPT (3 × 10⁻³ M) due to its lower solubility than the other tetrazines in CH₃CN, and 0.1 M NBu₄PF₆ was used as a supporting electrolyte.

Fabrication of DPT/CMK-3 Composites: The DPT/CMK3 composites were prepared by a simple method. DPT and CMK-3 (BET1000, 99%, ACS Material) were mixed in dimethylformamide (DMF) with various mixing ratios (DPT:CMK-3 = 1:2, 1:1, and 2:1 by weight, respectively). After ultrasonication for 1 h, the solvent of the mixed solutions was slowly evaporated overnight under the ambient condition. Then, the mixtures were placed in a vacuum oven to remove the residual solvents completely.

Cathode Fabrication and Galvanostatic Test: Slurries of the tetrazines, carbon black (Timcal Super P), and PVDF (Sigma Aldrich) in dimethylformamide (DMF) were prepared in a vial with a weight ratio of 4:4:2. For the DPT/CMK-3 composite electrodes, slurries were mixed with the DPT/CMK-3 composite materials, carbon black, and PVDF in a weight ratio of 8:1:1. The slurries were stirred overnight at room temperature and then spread on aluminum foils by doctor blading. The electrodes were dried at 25 °C for 8 h in a vacuum oven and punched into circular discs with a diameter of 14 mm. Coin type CR2032 (Hohsen) cells were assembled with the cathodes, a Li-metal anode, and a polypropylene separator (Celgard 2400) in an Ar-filled glove box (Korea Kiyon KK-011-AS) in which moisture and oxygen levels were tightly regulated under 0.5 ppm. The galvanostatic discharge/charge tests of the coin cells at different current densities (the C-rate of the tetrazine electrodes were calculated by their theoretical specific capacity values) were performed on a battery cycler (Wonatech WBCS3000L) at 30 °C.

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Layout 2:

FULL PAPER



Novel s-tetrazines for electrode-active materials in secondary battery are developed for the first time. Through ex-situ XPS analysis, the redox mechanism of the s-tetrazine electrodes during charge/discharge is studied. By fabricating nanocomposite with mesoporous carbon CMK-3 to prevent dissolution of the small s-tetrazines into the electrolyte, their potential applicability as electrode materials is explored.

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s-Tetrazines as a new electrodeactive material for secondary batteries