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Thiocarboxylate organic electrodes for ultrahigh capacity room temperature sodium ion battery

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Abstract: Organic room temperature sodium ion battery electrodes with carboxylate and carbonyl groups have been widely studied. Herein, for the first time, we report a family of sodium ion battery electrodes with stepwise substitution of oxygen in carboxylate group with sulfur, which improves electron delocalization, electrical conductivity and sodium uptake capacity. The versatile strategy based on molecular engineering can greatly enhance the specific capacity of organic electrodes with the same carbon scaffold. By introducing two sulfur atoms to a single carboxylate scaffold, the molecular solid can reach a reversible capacity of 466 mAh g^{-1} at current density of 50 mA g^{-1}, when four sulfur atoms are introduced, the capacity increases to 567 mAh g^{-1} at current density of 50 mA g^{-1}, which is the highest capacity value among reported organic sodium ion battery anodes until now.

Organic battery electrodes are alternatives to traditional metal oxide electrode materials due to their low cost, absence of heavy metals and easily tunable structures.[1-15] Generally, the organic electrodes accommodate redox and alkali metal ion insertion by functional groups such as carboxylate,[16] carbonyl,[17] organodisulfide,[18] thioether[19] and nitroxyl radicals,[20] while the aromatic cores donate or accept electrons during redox process.[19] Carboxylates are usually considered as lithium/sodium anodes by reversibly store/release Li$^+$/Na$^+$ through a two-electron process.[21,22] In the case of lithium ion anode, far more than two Li$^+$ ions can be stored in the molecule under deep discharge,[23,24] which leads to high capacity of organic lithium anodes. However, for sodium ion battery cells, there is no evidence of "super-sodiation" compared with lithium counterpart due to large sodium ion together with less electronegativity.

Even though organic sodium ion battery has lower specific capacity than lithium ion battery, it is attractive because of the less rigid lattice compared with metal oxides, which can accommodate the large sodium ions so that the rate capability and cycle stability can be possible advantages.[21] As a classic organic sodium ion battery anode, the sodium salt of terephthalate (PTA-Na, compound **a** in Figure 1) has a capacity of 295 mAh g^{-1} at current density of 0.1 C (30 mA g^{-1}),[16,21] which is comparable to the commonly available hard carbon anodes (≈ 280 mAh g^{-1}) with charge/discharge plateau of 0.3 V in half cell configuration.[25] Up to now, most of the organic sodium electrodes are composed of oxygen-containing functional groups (carboxylate and carbonyl groups).[21,26,27] The limitation of these functional groups is that they can only reversible store one sodium ions, which makes the capacity is strongly limited by the molecular weight of the molecule.[28] Another critical problem for organic battery electrodes is their poor conductivity, which limits the specific capacity, rate capability and cycle stability.[29] Commonly used electrode modification such as conductive carbon coating is difficult to realize, because most of the organic compounds decompose under high temperatures.[30] Apparently, increasing the number of sodium ion stored per molecule, as well as intrinsic conductivity by chemical modification for organic electrodes will significantly enhance the performance of organic batteries.

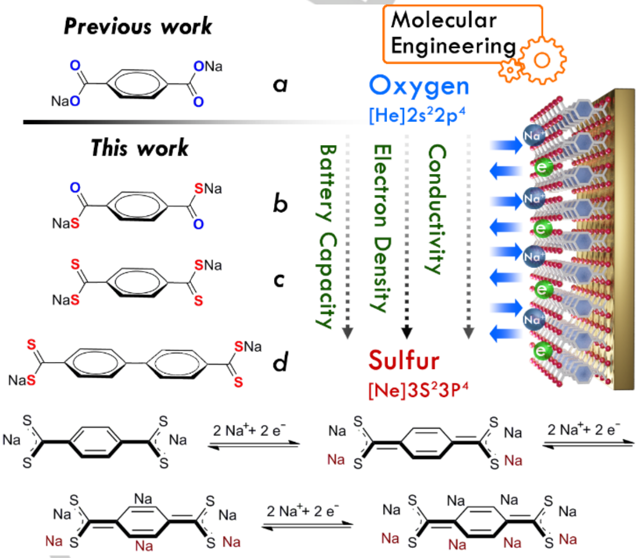

Figure 1. Schematic illustration of sulfur doping in molecular battery anode.

Recently, organic molecules with heteroatom-doping exhibited obvious advantages towards richer redox centers and higher electric conductivity. For instance, it is reported that nitrogen incorporation will enhance the electron density per mass.[31,32] Sulfur atom, which in the same group (Group VIA) as oxygen, larger atomic radius and electron density (atomic radius: 100 pm, [Ne]3s^{2}3p^4 for S) per molecule, evidently compared with oxygen atom (atomic radius: 60 pm, [He]2s^{2}2p^4 for O). Accordingly, atomically doping sulfur in organic electrodes can potentially

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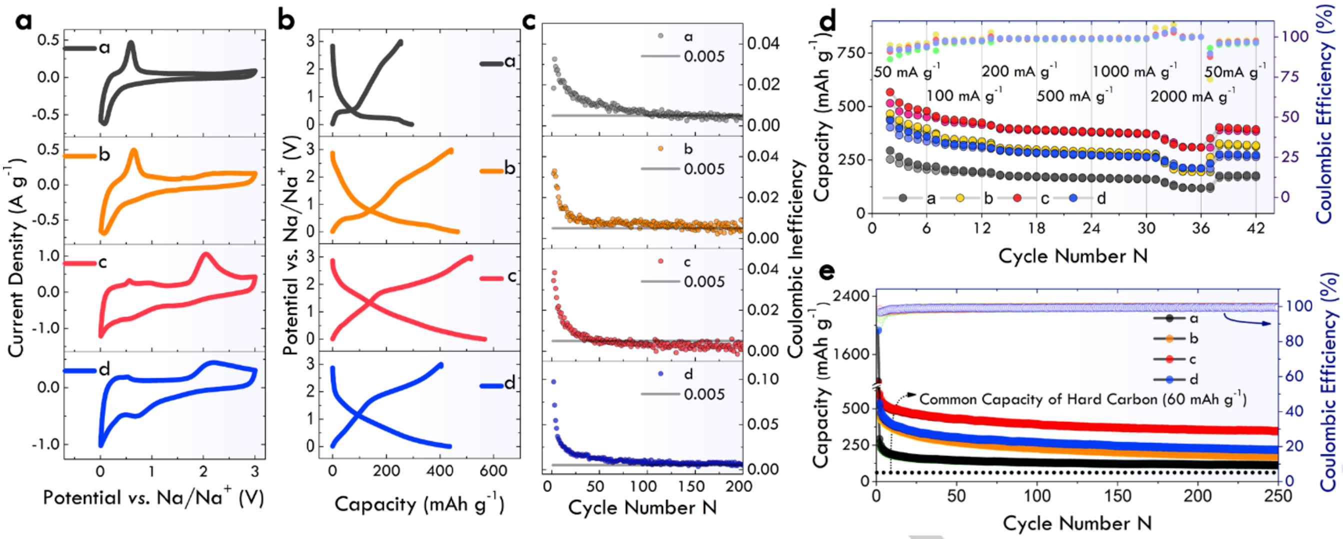

Figure 2. Electrochemical performance of the electrodes. (a) Cyclic voltammetry at scan rate of 0.2 mV s^{-1}. (b) Galvanostatic charge-discharge curves, (c) Coulombic inefficiency during 200 cycles. (d) Rate capability and (e) Cycle stability at 500 mA g^{-1}.

enhance the conductivity as well as store more sodium ions when sulfur is incorporated in the conjugated systems, and thus possibly deliver high specific capacity.[33]

Based on these considerations and molecular engineering techniques, the O atoms in PTA-Na molecule (**a**) were replaced by S atom in steps to give three sulfur-containing sodium salts (**b**, sodium 1,4-dithioterephthalate, **c**, sodium tetrathioterephthalate and **d**, sodium 4,4'-biphenyltetrathiodicarboxylate in Figure 1) by a facile one-pot method. It should be noted that we firstly successfully incorporated sulfur into the carboxylate groups to form sodium salts of **b**, **c**, as well as **d** and used as battery electrodes. The detailed synthesis procedure is listed in supporting information. The target compounds all precipitate out as molecular solids at room temperature.

We performed X-ray diffraction (XRD) measurement to study the crystallinity of the synthesized samples, the XRD pattern shows the significant difference in crystallinity among the samples (Figure S1 and S2). Scanning electron microscopy (SEM) images show that there is distinctive difference in the morphology of four samples. The morphology difference also implies the crystallinity of molecule **b**, **c** and **d** is not as good as molecule **a**. Besides, as mentioned above, electric conductivity is one of the most important factors in influencing the battery performance. Empirically, white samples are usually with poor electric conductivity due to their large band gap which makes the electron difficult to jump from valence band to conduction band. As expected, the color of the synthesized samples became darker with increasing sulfur content (Figure S3). The color change indicates not only the incorporation of sulfur atoms, but more importantly, the possibly increasing in electric conductivity. As it is expected, the measured conductivity of all-sulfur-substituted samples by four-probe test (Figure S5) are much higher than other two samples (0.01, 0.06, and 4.0 μS cm^{-1}), which is consistent with theory and Density Function Theory (DFT) calculations that the electrons are more delocalized on sulfur containing molecules. Besides, the band gap values are also in good accordance with the conductivity measurements (Table S1).

Four samples were tested as sodium ion battery anode in a coin cell with sodium metal as both counter and reference electrode. Notably, the electrodes barely dissolved in electrolyte (Figure S4). The redox peaks of the four samples against Na/Na$^+$ were characterized by cyclic voltammetry (CV) (Figure 2a). Interestingly, there are two types of cyclic voltammetry profiles for the molecular solids **a**, **b**, **c** and **d**: as for the molecules with oxygen atoms (**a** and **b**), the CV shows similar profile where the redox peak couple located at 0-0.5 V, while as for the molecules with solely sulfur atoms (**c** and **d**), the oxidation peaks appeared at 2.2 V, and reduction peaks located at 0.7 V. The distinct difference between two types of CV profiles is possibly derived from the different lowest unoccupied molecular orbital (LUMO) energy levels. Lower LUMO energy level caused by sulfur incorporation would result in higher redox potential. Notably, for the molecule with both oxygen and sulfur atoms (molecule **b**), besides the redox couple appeared at 0-0.5 V, there were also small but discernable oxidation and reduction peaks located at 2.2 and 0.7 V, respectively.

Galvanostatic charge-discharge curves for the four molecular compounds showed same trend as shown in CV measurements. The molecules with four sulfur atoms (**c** and **d**) exhibited a charge voltage plateau at 2.2 V, and the discharge curve showed a slope without significant discharge plateau. In contrast the molecules with one or two oxygen atoms (**a** and **b**) showed obvious plateau around 0.5 V. The slope-like discharge plateau for the molecules with four sulfur atoms is possibly attributed to the low crystallinity after initial discharge.[24] It can be seen from the charge-discharge curves that the discharge capacities at 50 mA g^{-1} for the four samples showed a trend that the increase number of sulfur atoms leads to higher capacity. Considering the low average voltage plateau and capacity, molecule **b** is a competitive material for sodium ion battery. The molecule with one phenyl group and four sulfur atoms (**c**) presented highest capacity of 567 mAh g^{-1} which is also the largest organic sodium battery electrode capacity among the reported literatures (Table

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S4). While the molecule with four sulfur atoms and biphenyl group (**d**) and molecule with two sulfur atoms and two oxygen atoms (**b**) have similar capacity (436 and 466 mAh g^{-1}). The molecule contains only oxygen atoms revealed lowest capacity of 294 mAh g^{-1}. The results indicated substituting sulfur with oxygen atom can significantly improve the capacity of the molecules. The rate performances of four molecules are shown in Figure 2d. The capacity of sulfur-substituted molecule electrodes exhibited much higher capacity compared with PTA-Na molecule at each current density. The excellent rate performance of the molecules suggested that the sulfur substitution can maintain a high capacity at high current rate, which is a reliable method for high-rate organic electrode design.

It is interesting to find that the molecules with sulfur were more stable than pure PTA (**a**). The capacity retention at 500 mA g^{-1} after 200 cycles are 40%, 40%, 60%, and 43% for **a**, **b**, **c**, and **d** respectively (Figure 2e). The initial irreversible capacity of molecule **a**, **b**, **c** and **d** are 82%, 66%, 66% and 83%, respectively (Figure S32). The Coulombic inefficiency (CI) was plotted for four molecules. It was found that for molecule **c**, the CI value decreased below 0.005 after 50 cycles, indicating the molecule has highly efficient charge-discharge behavior (Coulombic efficiency > 99.5%) when evaluated as sodium ion battery anode. Due to the outstanding performance, molecule **c** was selected as model for next analyses. dQ/dV study of molecule **c** revealed that during 200 cycles, the charge plateau remained unchanged, implying the redox reaction is highly reversible.[34]

In order to investigate the charge storage mechanism of the organic anodes, a series of cyclic voltammetry scans were taken from 0.2 to 5 mV s^{-1} to investigate the portion of capacitive contribution and diffusion controlled contribution.[35] The total current I is contributed by the sum of diffusion controlled current I_d and capacitive current I_c:

$$I = I_d + I_c$$

where I_d is proportional to the square root of scan rate and I_c is proportional to scan rate. Figure S28 a and b shows the I_d and I_c for molecule **a** and **c**. The portion of diffusion controlled capacity is similar (83% and 84%). Though for the molecule **c**, the 0-1.5 V region are rectangular-like, diffusion still controlled the electrochemical process, indicating battery-type process is taking place at the full range of electrochemical process.

Raman spectroscopy can investigate the structural change of the molecule during charge-discharge process.[36] In-situ Raman spectroscopy of molecule **c** was performed during the first discharge. The featured peaks of phenyl around 1600 cm^{-1} and C=S around 1200 cm^{-1} diminished with increasing the discharge depth, indicating the conjugated organic structure was changed (Figure 3a). Electrochemical impedance spectroscopy (EIS) measurement can be used to study the kinetics information with small stir in electrochemical cell.[37] The results showed that the contact resistance R_s and charge-transfer resistance R_{ct} of sulfur substituted molecule **c** is smaller than that of pure PTA-Na, which is consistent with conductivity measurement (Figure 3c and Figure S5, S30). These results further implied the capacity, cyclic stability can be enhanced when substituting sulfur with oxygen as the increased conductivity. As a proof of concept, we also fabricated a flexible cell to demonstrate its potential application in flexible bio-electronics (Figure 3d and Figure S33).

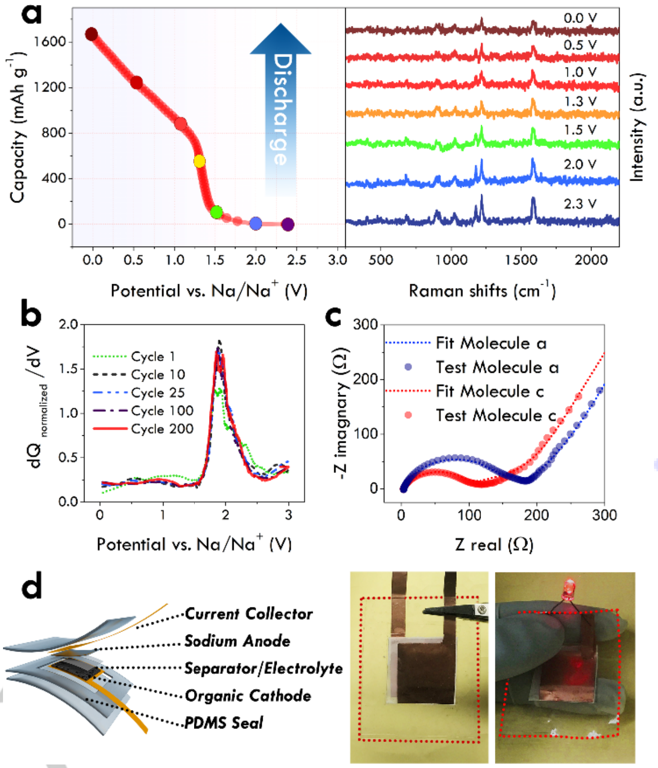

Figure 3. (a) In-situ Raman spectroscopy for the first discharge. (b) dQ/dV of 1st, 10th, 25th, 100th, and 200th cycles. (c) Capacitive and diffusion controlled contributions. (d) Prototype of a flexible organic battery.

From above results, the sulfur-incorporated molecules generally have better electrochemical performance. Higher electric conductivity allows faster electron transport that can compensate the charge-imbalance caused by redox reaction. More importantly, DFT calculation offered an important implication that the electron-rich sulfur substituted molecules has chance to reversibly store additional sodium ions during discharge.[38] As it is calculated by DFT (Figure 4 and Figure S34-35) that molecule **c** can uptake up to 6 additional sodium ions. The HOMO of molecule **c** with 4, 6, and 8 sodium ions still well localizes within the scaffold, indicating the sufficient stability of **c** and explaining the successful supersodiation process,[38] which is similar to "super-lithiation" in organic lithium battery electrodes.[23] Correspondingly, the theoretical capacities of the molecules are 255, 443, 586, and 459 mAh g^{-1} (Table S3). Interestingly, as it is implied by DFT calculations, different from PTA-Na, where the sodium ions are only stored at the carboxylate groups, the entire sulfur-substituted molecule becomes a "sodium reservoir". The sodium ions stabilized on both side of the benzene ring when the molecule uptakes 6 or 8 sodium ions. The additional sodium ions can be stored in molecule **c** instead of molecule **a** because the electron density is much higher for sulfur substituted molecules. The ^{1}H NMR study was used to get detailed information on the structural changes of the molecules. Compound **a** before discharge exhibits a single strong signal with a chemical shift of δ = 7.9 ppm. After discharging to 0 V, the aromatic proton reversibly shifts and splits into two peaks (δ = 6.5 and 6.7 ppm) (Figure S31). These results not only proved that the existence of aromatic structures, but also reflected the destruction of the symmetry of the aromatic system after the discharge process, which are consistent with our calculation results.

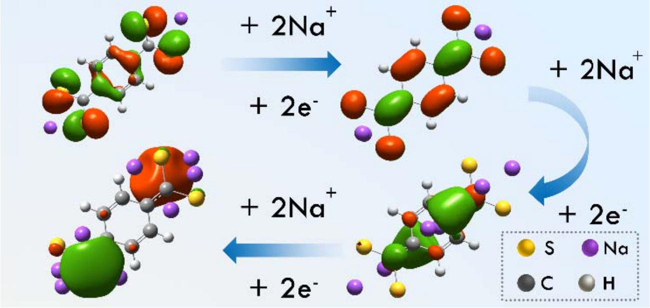

Figure 4. Calculated HOMO plots of molecule **c** with different sodium uptake amount.

In conclusion, we have developed a family of thiocarboxylate compounds for high capacity organic battery electrodes. The novel sulfur-substituted compounds can significantly enhance the capacity as well as cyclic stability compared with the traditional carboxylic acid based organic electrode. The capacity of the sulfur substituted molecule is as high as 567 mAh g^{-1} at the current density of 50 mA g^{-1} with high stability and rate performance. The increased capacity when substituting sulfur for oxygen was mainly derived from the decreased band gap and thus the greatly enhanced electric conductivity and the enhanced sodium ions uptake by high electron density aromatic rings. The versatile and efficient strategy offers new chances for developing next-generation high capacity sodium ion battery electrodes.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Main group elements • Conjugation • Organic battery

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Entry for the Table of Contents

COMMUNICATION

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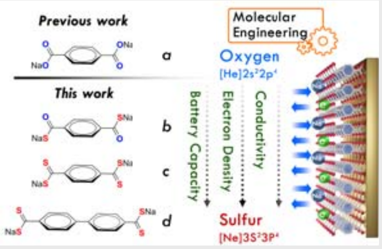

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