High Energy Organic Cathode for Sodium Rechargeable Batteries

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Supporting Information

ABSTRACT: Organic electrodes have attracted significant attention as alternatives to conventional inorganic electrodes in terms of sustainability and universal availability in natural systems. However, low working voltages and low energy densities are inherent limitations in cathode applications. Here, we propose a high-energy organic cathode using a quinone-derivative, $C_6Cl_4O_2$, for use in sodium-ion batteries, which boasts one of the highest average voltages among organic electrodes in sodium batteries (~ 2.72 V vs Na/Na⁺). It also utilizes a two-electron transfer to provide an energy of 580 Wh kg^{-1} . Density functional theory (DFT) calculations reveal that the introduction of electronegative elements into the quinone structure significantly increased the sodium storage potential and thus enhanced the energy density of the electrode, the latter being substantially higher than previously known quinone-derived cathodes. The cycle stability of $C_6Cl_4O_2$ was enhanced by incorporating the $C_6Cl_4O_2$ into a nanocomposite with a porous carbon template. This prevented the dissolution of active molecules into the surrounding electrolyte.

The development of electrochemical systems that can provide clean and efficient routes for energy storage is becoming more important than ever. Since their introduction by Sony in 1991,¹ lithium-ion batteries (LIBs) have been used widely in commercial power sources for portable electronics. In recent years, LIB technology has expanded to large-scale energy storage systems (ESSs), such as those used in electric vehicles and stationary storage devices in conjunction with the energy harvesting from renewable energy sources, i.e., solar, wind, and geothermal energies. Nevertheless, several practical issues have yet to be resolved, such as insufficient energy/power density, inefficient cycle performance, and high cost for large scale applications. In particular, cost issues become more challenging as LIB technology is applied to large-scale systems. The relatively high cost of LIBs is due primarily to the use of expensive transition metals such as cobalt and nickel.^{2,3} In addition, the limited availability of Li resources in small regional areas is a growing concern as Li demand increases.^{4,5} In light of these problems, sodium-ion batteries (SIBs) have recently been rehighlighted as alternative battery systems.^{6,7} The abundance of Na resources and the electrochemical similarities between Na and Li make SIBs more attractive as performance per capital becomes a decisive factor, particularly in large scale ESSs.^{6–9}

Organic electrodes have attracted a great deal of attention as substitutes for conventional electrodes based on transition metal redox chemistry.¹⁰ The absence of a transition metal in

the electrode material assures greater cost-effectiveness. Recently discovered bioinspired organic electrodes, such as those composed of carbonyl, carboxyl, and quinone-based materials, promise additional merits of sustainability, universal availability in natural systems, and reduced carbon footprint synthesis.^{11–15} More recently, quinone-derivatives that imitate redox-active plastoquinone and ubiquinone cofactors have shown significant improvement with regard to their performance in rechargeable batteries.^{16–22} These quinone derivatives have the potential to deliver specific capacities^{22–27} comparable to those of state-of-the-art inorganic electrode materials,^{28–30} but with metal-free C=O redox centers. While there have been extensive investigations on quinone-based cathode materials for NIBs,^{31–34} the inherently low working potential (<2.5 V vs Na/Na⁺) still remains a primary obstacle to realizing high energy quinone-based cathodes.

A promising means of tuning this working potential is to modify the elemental species in the quinone derivatives while maintaining the electroactivity of the C=O redox centers. Recently, Yokoji et al.³⁵ reported that benzoquinones bearing perfluoroalkyl groups exhibited high average discharge voltages (3.1 V vs. Li/Li⁺) in LIBs. However, the increase in molecular

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Figure 1. Energetics of $C_6R_4O_2$ molecules ($R = F, Cl, Br$) using DFT calculations. (a) Chemical structure of $C_6R_4O_2$ molecules. (b,c) LUMO energies of $C_6R_4O_2$ molecules.

Figure 2. Theoretical DFT calculations on $C_6Cl_4O_2$ molecule and the electrochemical properties of $C_6Cl_4O_2$ cathode. (a) HOMO/LUMO levels of $C_6R_4O_2$ and $[C_6R_4O_2]^{2-}$ ($R = Cl, Br, F$). (b) Typical charge/discharge profile of $C_6Cl_4O_2$ at 10 mA g⁻¹. (c) Capacity vs. voltage plots of $C_6Cl_4O_2$ and other organic cathode materials in LIBs and SIBs. The operation voltage (vs Na or Li) and theoretical capacity were used to calculate the energy density. (d) Natural bond orbital analysis. (e) DFT energy comparison for various forms of $NaC_6Cl_4O_2$.

weight due to the long alkyl chains considerably reduced specific capacities and resulted in overall low energy densities. In this work, we believed that substitution with halogen atoms such as fluorine and chlorine should increase the redox potential of benzoquinone derivatives without increasing their molecular weight. The relatively high electronegativity of the halogen groups would draw electrons from the molecule, thereby increasing the redox potential of the C=O redox centers. This approach using electron withdrawal from active redox centers is analogous to the well-known inductive effect observed in inorganic cathode materials, such as $LiFePO_4$ and $LiFeSO_4F$.^{28,36,37} In accordance with this strategy, we propose a new, high-voltage cathode of tetrachloro-1,4-benzoquinone ($C_6Cl_4O_2$) for use in SIBs. The $C_6Cl_4O_2$ cathode exhibits an average redox potential of 2.72 V (vs. Na/Na⁺), which is substantially higher than those of similar systems.^{22–27}

In order to examine the effect of substitution on redox potential, we performed a theoretical investigation of quinone derivatives bearing various species (F, Cl, or Br) and numbers of electron-withdrawing halogen atoms, as illustrated in Figure 1a. All calculations were performed in the environment of dielectric constant = 70. (For more detailed information, see Calculation Details and Table S1 in Supporting Information.) It is well-known that there is a linear relationship between the redox potential and LUMO level (or reduction energy of molecules), especially among the molecules with similar structures.^{38,39} Note that precise prediction of the redox potential in organic molecules is challenging because the detailed crystal structures of organic molecules with/without guest ion are seldom known.^{38,39} Our DFT calculations show that lowest unoccupied molecular orbital (LUMO) energy decreases with the addition of halogen groups (Figure 1b,c).

Note that the substitution of one hydrogen atom in benzoquinone for one halogen atom results in a ~ 0.2 eV downshift in the LUMO energy. Approximately the same shift was observed with additional substitutions, although the magnitude of the shift per substitution was reduced at higher halogen content. Our calculations indicated that the decrease in LUMO energy was the greatest after substitution with fluorine and to a lesser extent following substitution with chlorine. Since the redox potential of an organic electrode is generally proportional to its LUMO energy,^{15,38} the Na storage potential of benzoquinone via $C=O$ redox centers is expected to increase with the substitution of hydrogen atoms for halogens. According to our calculation, redox potentials should follow the trend $C_6F_4O_2 > C_6Cl_4O_2 > C_6Br_4O_2 > C_6H_4O_2$.

Among them, two molecules with the highest expected redox potentials, $C_6Cl_4O_2$ and $C_6F_4O_2$, were selected as candidates for use in SIBs. Before experimental characterization, the Na storage capabilities of $C_6Cl_4O_2$ and $C_6F_4O_2$ were prescreened computationally by investigating LUMO level of neutral $C_6R_4O_2$ and $[C_6R_4O_2]^{2-}$ with respect to Na/Na^+ redox potential. Na/Na^+ redox potential was set to -1.7 V (corresponding to -1.7 eV because of the one electron transfer) since standard hydrogen electrode (SHE) is -4.4 V vs absolute vacuum scale (AVS) and Na/Na^+ is -2.7 V vs SHE.^{40,41} As shown in Figure 2a, neutral $C_6R_4O_2$ molecules can get electrons from Na/Na^+ redox couple (-1.7 eV) because LUMO levels are located at -4.6 to -5.1 eV, while $[C_6R_4O_2]^{2-}$ molecules cannot obtain more electrons due to higher LUMO levels, which are located at -0.6 to -1.4 eV. Therefore, it can be speculated that $C_6R_4O_2$ molecules can bear no more than two electrons in their structure. The result was again confirmed by the visualization of highest occupied molecular orbitals (HOMO) density. HOMO density of $[C_6R_4O_2]^{2-}$ was confined in the molecule structure, while that of $[C_6R_4O_2]^{4-}$ is located outside of molecules, which means that additional electrons cannot be stabilized in the molecule structure (Figure S1). It should be noted that the HOMO/LUMO calculation can only be applied to roughly estimate the properties of electrode materials, i.e., redox potential and capacity, but do not represent the theoretically rigorous quantitative values.

Galvanostatic measurements were performed to verify the Na storage capability of the electrodes. The $C_6Cl_4O_2$ and $C_6F_4O_2$ powders were purchased from Sigma-Aldrich and used without further purification. The electrochemical analysis was carried out using coin-type cells at $30^\circ C$. The amount of the active materials per electrode was 3–4 mg. Figure 2b shows that $C_6Cl_4O_2$ delivered a reversible capacity of ~ 150 mAh g^{-1} , corresponding to ~ 1.4 Na^+/e^- insertion per molecule at a current rate of 10 mA g^{-1} . Two distinct redox plateaus were observed at 2.9 V (vs. Na/Na^+) and 2.6 V (vs. Na/Na^+), with respectably small polarization. Figure S2 shows that $C_6F_4O_2$ delivered a similar discharge capacity of ~ 140 mAh g^{-1} with a single redox plateau at 2.9 V (vs. Na/Na^+). Note that an unsubstituted $C_6H_4O_2$ electrode in a lithium cell has a redox potential of 2.7 V (vs. Li/Li^+), which corresponds to 2.4 V (vs. Na/Na^+) in a sodium cell.⁴² The observed increase in potential with substitutions by Cl and F agrees with our prediction that halogen elements can upshift the voltage of the electrode effectively. Note also that an F substitution raised the redox potential slightly more than a Cl substitution. This is consistent with the data in Figure 1c, which shows that the LUMO energy reduction was greater with F (-5.06 eV) than with Cl (-4.84 eV). However, $C_6F_4O_2$ did not show a reversible charge

capacity after the initial discharge. This might be due to the chemical instability of sodiated $C_6F_4O_2$ in the presence of an organic electrolyte during charging.

The electrochemical reaction at the $C_6Cl_4O_2$ electrode included ~ 1.4 sodium atoms, yielding an estimated energy density of ~ 405 Wh kg^{-1} . At upper plateau, ~ 0.86 electron transfer (close to 1 electron transfer) occurs in the $C_6Cl_4O_2$ electrode, while ~ 0.56 electron passes at lower plateau (Figure S3). We believe that less specific capacity than the theoretical value of 2 electron transport is attributable to (i) the low electronic conductivity of $C_6Cl_4O_2$ and (ii) Na – Na repulsion in the last stage of the discharge. In Li cells, a specific capacity of ~ 164 mAh g^{-1} was obtained, corresponding to 1.54 electron transfer. A slightly higher capacity in Li cells is attributable to weaker Li – Li repulsion than Na – Na repulsion in the discharged state.

Given the redox potential of the electrode and its maximum occupancy of two sodium atoms, the theoretical energy density of $C_6Cl_4O_2$ can reach 580 Wh kg^{-1} (see Figure 2c), which is comparable to the theoretical energy density of a $LiFePO_4$ cathode (~ 587 Wh kg^{-1}).⁴³ Further improvements in the electrode and the overall battery system are required to yield optimal performance of a $C_6Cl_4O_2$ cathode. Nevertheless, it is notable that the average redox potential of $C_6Cl_4O_2$ (~ 2.72 V vs. Na/Na^+) is exceptionally high relative to those of previously characterized organic cathode materials, including both SIBs and LIBs.^{22–27} To our knowledge, this is the highest redox voltage that has been attained in organic SIB electrodes. Additional natural bond orbital (NBO) analysis revealed that $C=O$ bonds in $C_6Cl_4O_2$ was converted to $C-O$ bonds when reduced during the cell reaction, forming benzene-like conjugation structure in carbon ring (Figure 2d). The reaction can be categorized by type-3 “conjugated carbonyl reaction” in previous work,³⁸ of which high redox potential is known to be originated from the formation of stable benzene ring. We also confirmed that the most stable Na storage configuration is in the vicinity of oxygen atom of $C_6Cl_4O_2$, minimizing electrostatic energy (Figure 2e).

To better understand the redox reaction mechanism of $C_6Cl_4O_2$ electrodes, we monitored the change of valence states of O and Cl using ex situ XPS analysis (Figure 3). For the preparation of samples, the electrodes were cycled with a

Figure 3. Ex situ XPS analysis of $C_6Cl_4O_2$. (a) Typical charge/discharge profile. XPS peaks of (b) Na_{1s} , (c) O_{1s} , and (d) Cl_{2p} during Na insertion and extraction.

Figure 4. Origin of capacity degradation upon repeated battery cycles. (a) Charge/discharge profiles at various voltage ranges and cycle stability at various voltage ranges (inset). (b) Photo image of the electrolytes before and after battery cycles. (c) Absorbance spectroscopy after battery cycles at different voltage ranges.

constant current of 20 mA g⁻¹. In C₆Cl₄O₂, O_{1s} peak was gradually shifted to lower binding energy, indicative of the reduction of oxygen upon discharge. Note that a peak evolved at ~536 eV in O_{1s} is the Na KLL Auger peak. Simultaneously, Cl_{2p} peaks were slightly shifted to lower binding energy and a new peak at ~198 eV evolved, corresponding to the electron accommodation in chlorine and the binding between Na and Cl. It is originated from the Na insertion in the structure of C₆Cl₄O₂, which binds with Cl. This result is in a good agreement with our DFT calculations, which revealed that the most stable Na storage configuration in C₆Cl₄O₂ allows the redox reaction primarily at the oxygen and chlorine atoms. After charge, the valence states of O_{1s} and Cl_{2p} were reversibly recovered maintaining the bonding characteristics with carbon framework in C₆Cl₄O₂. However, a slight irreversibility in O_{1s} environment was observed comparing to the pristine electrode after a cycle, which may result in the minor capacity degradation.

On the contrary, we found that the Na incorporation into C₆F₄O₂ electrodes results in the irreversible formation of NaF compound instead of bonding of Na at F within the C₆F₄O₂ framework (Figure S4). Upon discharge, the Na_{1s} peak evolved and O_{1s} peak was shifted to lower binding energy indicating that the oxygen contributes as a redox center. Difference from the former case, however, is that no noticeable shift of F_{1s} peak was observed. The F_{1s} peak at ~688 eV was simply diminished and a new peak at ~684 eV, corresponding to NaF, appeared, which resembles the nature of the two-phase reaction. In contrast to Cl, which showed a clear shift of binding energy, i.e., redox activity in C₆Cl₄O₂, F irreversibly detaches from the C₆F₄O₂ structure and forms NaF compound. The precise reason for this difference is not clearly understood yet, but it is speculated to be related with the higher polarizability of the Cl than F. After charge, the chemical environments were not recovered, indicating the irreversibility of NaF formation upon discharge.

Figure 4a shows the cycle performance of C₆Cl₄O₂ cathodes in various voltage ranges. When the C₆Cl₄O₂ cathode is cycled between 2.0 and 3.5 V (vs. Na/Na⁺), the capacity decays rapidly. Similar behavior was observed when cycling only with the upper plateau region between 2.6 and 3.5 V (vs. Na/Na⁺). However, slightly better cycle performance was observed when the cutoff voltage was decreased to 2.9 V (vs. Na/Na⁺), which includes only the lower plateau. In order to understand the origin of capacity degradation upon battery cycling, we examined the chemical stability and the dissolution properties of the C₆Cl₄O₂ cathode in the electrolyte (Figures S5 and S6). Most organic electrodes suffer from rapid cycle deterioration due to chemical instability and dissolution of the electrode itself in organic electrolytes.^{10,14,44–46} First, we confirmed the chemical stability of as-prepared C₆Cl₄O₂ molecules in a surrounding electrolyte (Figure S5), which showed no evolution of second phases other than C₆Cl₄O₂ powders after more than a day storage in the electrolyte. Second, when the C₆Cl₄O₂ electrode was stored in a carbonate-based electrolyte for 12 h, it was found that the colorless electrolyte became yellow (Figure S6a).

After the color change, the electrolyte was analyzed with Fourier transform infrared spectroscopy (FTIR). Several new peaks were detected in the FTIR as shown in Figure S6b. These new peaks were consistent with those of C₆Cl₄O₂ molecules, indicating the dissolution of the electrode material into the electrolyte. Dissolution was even more prevalent when the C₆Cl₄O₂ cathode was cycled with a high voltage cutoff (3.5 V vs. Na/Na⁺). When the electrode was cycled between 2.6 and 3.5 V (vs. Na/Na⁺), the color of the electrolyte became a deeper yellow than was observed when using a lower cutoff voltage range (2.0–2.6 V vs. Na/Na⁺), as shown in Figure 4b. Moreover, an absorbance peak near 340 nm, which is characteristic of C₆Cl₄O₂, in the electrolyte grew notably for electrode that was cycled between 2.6 and 3.5 V (vs. Na/Na⁺), compared to that cycled at a lower voltage range (Figure 4c).⁴⁷

$C_6Cl_4O_2$ electrodes at various SOC (state of charges; as-prepared $C_6Cl_4O_2$, $NaC_6Cl_4O_2$ (half discharged), $Na_2C_6Cl_4O_2$ (fully discharged), and cycled $C_6Cl_4O_2$) were also stored in the electrolyte for the stability check (Figure 5). While less change

Figure 5. Dissolution tests of $C_6Cl_4O_2$ and its discharged and recharged states.

in color of the electrolyte was observed when as-prepared $C_6Cl_4O_2$ electrode or $Na_2C_6Cl_4O_2$ (fully discharged) sample was stored, the color of the electrolyte became deep yellow when $NaC_6Cl_4O_2$ (half discharged) or recharged samples (cycled $C_6Cl_4O_2$) were stored even after 4 h. It indicates that the dissolution loss became severe when the $C_6Cl_4O_2$ is recharged compared to the pristine state. It is presumably due to the partial phase transition of the electrode after cycles as indicated by the irreversible change in O_{1s} environment shown in Figure 3. Considering the case that the $C_6Cl_4O_2$ is cycled at lower voltage range involving two phases of $NaC_6Cl_4O_2$ and $Na_2C_6Cl_4O_2$, only the $NaC_6Cl_4O_2$ sample at charged state would dissolve in the electrolyte. However, when the cycling is carried out at the upper voltage region involving cycled $C_6Cl_4O_2$ and $NaC_6Cl_4O_2$, both of the discharged sample ($NaC_6Cl_4O_2$) and recharged sample ($C_6Cl_4O_2$) would undergo the significant dissolution in the electrolyte. As a result, cycling at a higher voltage plateau leads to a more rapid dissolution over cycles and shows worse cycle performance. These results suggest that dissolution of the active electrode molecules into the electrolyte is a major reason for capacity degradation.

To suppress the dissolution of $C_6Cl_4O_2$ into the electrolyte, we attempted to confine the active electrode molecules by sequestering them within mesoporous carbon (CMK). This concept was inspired by a recent work with Li-sulfur batteries in which polysulfide dissolution is problematic (Figure 6a).⁴⁸ $C_6Cl_4O_2$ powder was dissolved in dimethylformamide (DMF) and mixed with CMK powder to prepare $C_6Cl_4O_2$ /CMK composites. $C_6Cl_4O_2$ molecules were drawn into the CMK by capillary effects during the slow evaporation of the DMF solvent.⁴⁸ The detailed characterizations of $C_6Cl_4O_2$ /CMK composite are shown in the Supporting Information (Figures S7–S11). After sequestration in CMK, the cycle performance of $C_6Cl_4O_2$ electrode was reexamined. A slightly higher capacity ($\sim 161 \text{ mAh g}^{-1}$ corresponding to 1.5 Na per f.u.) was obtained, most likely due to the higher electrical conductivity of the CMK as shown in Figure 6b. Note that the specific capacity is calculated on the basis of $C_6Cl_4O_2$ mass only, and a small additional capacity comes from the CMK component (Figure S12). Figure 6c shows that the cycle stability was enhanced noticeably relative to that of a $C_6Cl_4O_2$ electrode mixed with conductive carbon in the full voltage range operation, from 2.0 to 3.5 V.

However, capacity degradation was still observed since dissolution could not be prevented completely by CMK

Figure 6. Fabrication of $C_6Cl_4O_2$ /CMK composite and its electrochemical properties. (a) Schematic illustration of fabrication process of $C_6Cl_4O_2$ /CMK composite. (b) Typical charge/discharge profiles of $C_6Cl_4O_2$ (upper) and $C_6Cl_4O_2$ /CMK (lower). (c) Cycle performance of $C_6Cl_4O_2$ and $C_6Cl_4O_2$ /CMK.

sequestration. Some previous papers described the significant improvement of electrochemical performance in Li-organic systems when CMK was utilized.^{49–51} However, our system did not provide such a great improvement different from the previous literatures. It is attributable to smaller molecule size of our proposed electrode material. The π - π interaction between organic molecules and carbon materials (here, CMK) generally inhibits the dissolution of molecules into the electrolyte.⁵² However, the effect reduces when the number of benzene moieties in the organic molecules decreases due to the effectively smaller π - π interaction. Smaller molecules are more easily dissolved in the electrolyte despite the infiltration in CMK because of the weak interaction between active organic molecules and CMK. In addition, different solvation characteristics in Li and Na systems can affect the dissolution loss of active organic molecules while further study is required. Na ions are less strongly solvated with electrolyte solvents,⁵³ as a result, more free solvents that can dissolve the active organic molecules are formed. This difference might affect the worse cycle performance in the Na-organic system.

In order to maintain stable cycle retention in these organic systems, a new strategy is required to block electrode dissolution effectively. Such a strategy will be universally beneficial for the utilization of organic electrodes in rechargeable ion batteries and for sulfur electrodes in lithium sulfur batteries. In other respects, it is expected that the high voltage quinone-derivate cathode can be applied as a candidate for flow battery systems. Recently, there have been much attention on quinone-flow batteries taking advantage of the intrinsic dissolution properties of the quinone in the solvent; this battery system uses solutions of quinone derivatives as redox active materials.^{54–57} The dissolution of $C_6Cl_4O_2$ in the electrolytes would be beneficial for the application in such quinone-flow battery systems, while further searches for appropriate electrolytes are required.

In summary, we proposed quinone derivative ($C_6R_4O_2$) containing electron-withdrawing elements ($R = Cl$) as a novel, high-energy organic cathode for SIBs. The introduction of electronegative elements lowered the LUMO energies of the quinone derivatives, which in turn increased their Na storage

potential. A rationally designed cathode ($\text{C}_6\text{Cl}_4\text{O}_2$) exhibited an average voltage of ~ 2.72 V (vs. Na/Na^+), which is considerably higher than those of reported organic cathode materials.^{22–27} Experimentally, the $\text{C}_6\text{Cl}_4\text{O}_2$ electrode could deliver a capacity of 161 mAh g^{-1} and an energy density of 420 Wh kg^{-1} with a theoretical energy density of 580 Wh kg^{-1} , which is the highest value yet attained with quinone-derived cathode materials. Overcoming the degradation of capacity coming from the dissolution of the electrode material into the surrounding electrolyte will make $\text{C}_6\text{Cl}_4\text{O}_2$ electrodes a promising low-cost, high-energy alternative for use in SIBs.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental details, calculation details, and supporting figures (PDF)

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All authors discussed results and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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