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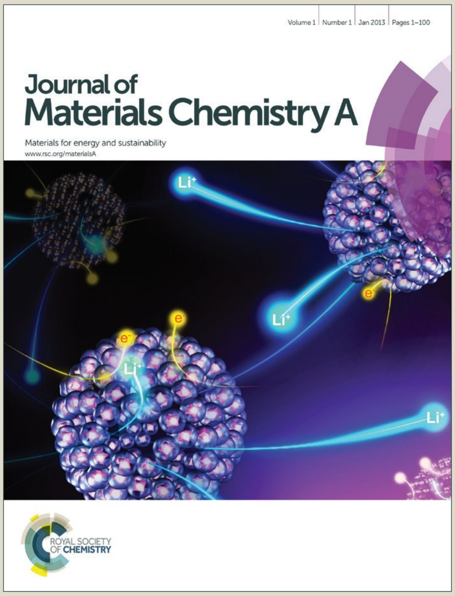

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ARTICLE

High-capacity organic cathode active materials of 2,2′-bis-*p*-benzoquinone derivatives for rechargeable batteries

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Rechargeable batteries using organic cathode materials are expected to afford high mass energy densities since the materials can undergo multiple electron redox reactions per molecule. Although the batteries using benzoquinone (BQ) derivatives as organic cathode active materials exhibited high theoretical capacity, their practical capacities and cycle retention were far from satisfactory. To overcome these problems, dimeric BQ derivatives based on the 2,2′-bis-*p*-benzoquione (BBQ) framework were synthesized, and the charge-discharge behaviour of prepared cells using BBQs as the cathode active materials was investigated. The BBQ-based cells exhibited excellent performance compared to those based on the BQ monomers. For example, the BBQ cell afforded a high initial capacity of 358 Ah kg^{-1} (more than twice that of current lithium-ion batteries that use $LiCoO_2$ as the cathode active material) and a high cycle retention of 198 Ah kg^{-1} at 50 cycles. Electrochemical measurements and density functional theory (DFT) calculations indicated that three electron-redox reactions generally occur in BBQ derivatives, although $(OMe)_2$-BBQ appeared to undergo a four-electron redox reaction.

Introduction

Currently, rechargeable lithium-ion batteries (LIBs) that use inorganic cathode active materials excel in volume energy density, which means that they are suitable for compact devices such as mobile phones and tablet devices.[1] However, as our dependence on portable powered devices evolves, the science to provide mass energy densities must also mature; batteries with high safety and mass energy densities are required for applications in emergency electrical storage systems and electric vehicles.[2] Whereas new types of rechargeable batteries using inorganic cathode active materials and with high safety and output voltage have been reported,[3] significant improvement in the mass energy density of these active materials is difficult, because they undergo single-electron transfer processes and have relatively low mass capacities. Therefore, organic cathode materials, which can undergo multiple electron transfers per molecule, are attractive in terms of their high mass energy densities compared to the inorganic types.[4] Furthermore, the use of organic cathode active materials produces low-cost, environmentally compatible, and safe batteries. Although $LiCoO_2$ is generally utilized as a cathode material in classic LIBs, the rare metal cobalt has several drawbacks. For example, it is a limited material resource, the disposal of LIBs using $LiCoO_2$ is costly and environmentally detrimental, and the tendency to overcharge or short-circuit poses potential safety risks.

Considering the advantages of the batteries that use organic cathode active materials, the development of rechargeable organic batteries would be desirable. Polymer cathode materials have been the main focus for organic battery research[4] because of their generally high cycle retention. However, polymers often provide lower capacities than the theoretical values calculated from their monomer units.[5] On the other hand, cells using low-molecular-weight organic cathode materials tend to exhibit high initial capacities but low cycle retention compared to the polymer cathode materials. Several studies to suppress the capacity degradation of low-molecular-weight organic compounds during cycling have recently been reported, in which new battery systems such as quasi-solid state[6] and two-compartment batteries[7] produced remarkable cyclability improvements. Therefore, the area of low-molecular-weight organic cathode materials is well worth investigating, and the development should contribute to the improvement of the mass energy density in rechargeable batteries.

The reported low-molecular-weight organic cathode materials can be classified into three groups: organosulfur,[8] radical,[9] and carbonyl compounds.[10,11] We have investigated the use of carbonyl-type 1,4-benzoquinone (BQ) derivatives as positive electrode active materials for rechargeable batteries,[12] which can afford high theoretical capacities (C_{theo}) due to their

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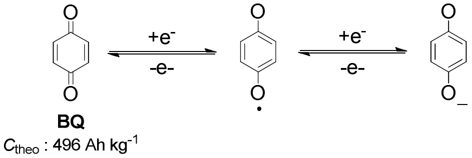
low molecular weight and two-electron-transfer capacity per molecule (Scheme 1). Our previous studies revealed that substituents on the BQ skeleton greatly affect battery performance; their electronic[12a] and steric effects[12b] are closely related to the discharge voltage and cyclability for the cells, respectively (Fig. 1). Specifically, the electron-deficient CF_3-BQ cell exhibited a high discharge voltage of 3.0 V *versus* Li/Li^+, whereas the electron-rich Me_2-BQ and DMBQ cells exhibited low discharge voltages of 2.7 and 2.6 V *versus* Li/Li^+, respectively.[12a] On the other hand, a cell using *t*Bu_2-BQ, bearing bulky *tert*-butyl groups, afforded high cycle retention (the ratio of the capacity at the 15th cycle to the 1st was 96%), whereas cells using Me_2-BQ, bearing less bulky methyl groups, afforded poor cycle retention (the ratio of the capacity at the 15th cycle to the 1st was 32%).[12b] In other words, the introduction of electron-withdrawing and bulky functional groups into the BQ skeleton improves the discharge voltage and cyclability for the cells, respectively. However, the introduction of numerous or high-molecular-weight functional groups into the BQ skeleton significantly decreases the theoretical capacity. For example, the theoretical capacity of perfluorobutyl-substituted BQ (C_4F_9-BQ) is 99 Ah kg^{-1}, which is much smaller than that of the non-substituted BQ (496 Ah kg^{-1}), and even lower than the practical capacity of $LiCoO_2$ (150–170 Ah kg^{-1}). Thus, we focused on the dimerization of the BQ skeleton to improve capacity while retaining high cyclability. Herein, we report a study of new carbonyl-type cathode active materials, 1,4,5,8-naphthodiquinone (NDQ) and 2,2′-bis-*p*-benzoquinone (BBQ) derivatives, for rechargeable lithium batteries; NDQ, BBQ, and R_2-BBQ (R = F, Cl, Br, Me, *i*Pr, *n*Bu, *t*Bu, OMe) were prepared and incorporated into battery cells for evaluation (Fig. 2). NDQ and BBQ afforded high theoretical values of 570 and 501 Ah kg^{-1}, respectively, which were based on the prediction that four-electron redox reactions would occur due to the four carbonyl units per molecule (Scheme 2). To the best of our knowledge, the use of NDQ and BBQ derivatives for cathode materials in rechargeable batteries has never been reported.



Scheme 1 Reversible redox reactions of BQ.

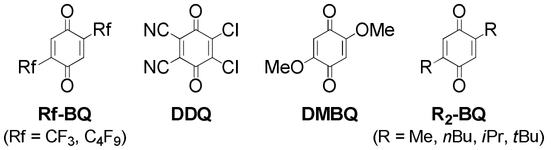


Fig. 1 Benzoquinones previously utilized as cathode active materials for LIBs.

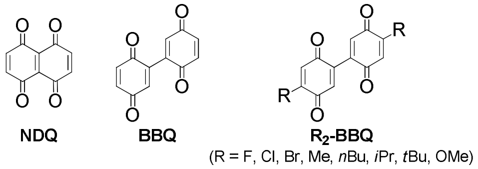
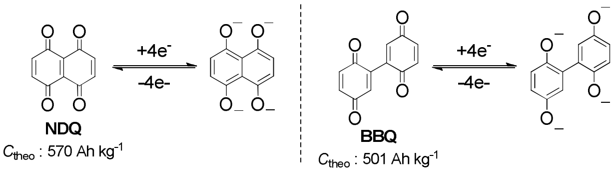


Fig. 2 Structures of NDQ and BBQ derivatives.



Scheme 2 Predicted reversible redox reactions involving four electrons for NDQ and BBQ.

Experimental

Preparation of NDQ and BBQ derivatives

1,4,5,8-naphthodiquinone (NDQ), 2,2′-bis-*p*-benzoquinone (BBQ), 5,5′-difluoro-2,2′-bis-*p*-benzoquinone (F_2-BBQ), 5,5′-dichloro-2,2′-bis-*p*-benzoquinone (Cl_2-BBQ), 5,5′-dibromo-2,2′-bis-*p*-benzoquinone (Br_2-BBQ), 5,5′-dimethyl-2,2′-bis-*p*-benzoquinone (Me_2-BBQ), 5,5′-dibutyl-2,2′-bis-*p*-benzoquinone (*n*Bu_2-BBQ), 5,5′-diisopropyl-2,2′-bis-*p*-benzoquinone (*i*Pr_2-BBQ), 5,5′-di-*tert*-butyl-2,2′-bis-*p*-benzoquinone (*t*Bu_2-BBQ), and 5,5′-dimethoxy-2,2′-bis-*p*-benzoquinone ($(OMe)_2$-BBQ) were synthesized according to the procedure outlined in Scheme 3 (for details of the synthesis, see the Supplementary Information, ESI), and the other BQs were purchased, which were used without further purification except BQ; BQ was purified by recrystallization from methanol.

NDQ[13] was prepared from 5,8-dihydroxy-1,4-naphthoquinone (**1**) through oxidation with [bis(trifluoroacetoxy)iodo]benzene in 15% yield. BBQ[14] was prepared from 1,4-dimethoxybenzene (**2**) through iodination using iodine and iodic acid,[15] followed by the Ullmann coupling in the presence of copper and 2,2′-bipyridine (bpy)[16] in 74 and 66% yields, respectively. Oxidation with cerium ammonium nitrate (CAN) afforded BBQ in 68% yield.[17] F_2-, Cl_2-, Br_2-, Me_2-, and $(OMe)_2$-BBQ were synthesized from 1,4-dimethoxy-2-fluorobenzene (**5**), 1,4-dimethoxy-2-chlorobenzene (**6**), 1,4-dimethoxy-2-bromobenzene (**7**), 1,4-dimethoxy-2-methylbenzene (**8**), and 1,2,4-trimethoxybenzene (**9**) through CAN oxidation in 39, 31, 25, 68, and 7% yields, respectively.[18] *n*Bu_2-BBQ was synthesized from **2** by introducing *n*-butyl groups using *n*-butyl lithium, tetramethylethylenediamine (TMEDA), and *n*-butyl bromide in 22% yield,[19] followed by oxidation with CAN in 83% yield.[18] *i*Pr_2-BBQ was also prepared from **2** in three steps, by introducing an α-hydroxyisopropyl group using *n*-butyl lithium and acetone in 47% yield, then dehydroxylation with palladium on carbon and sulfuric acid[20] in 79% yield, followed by CAN oxidation[18] in 81% yield. *t*Bu_2-BBQ was prepared from 2-*tert*-

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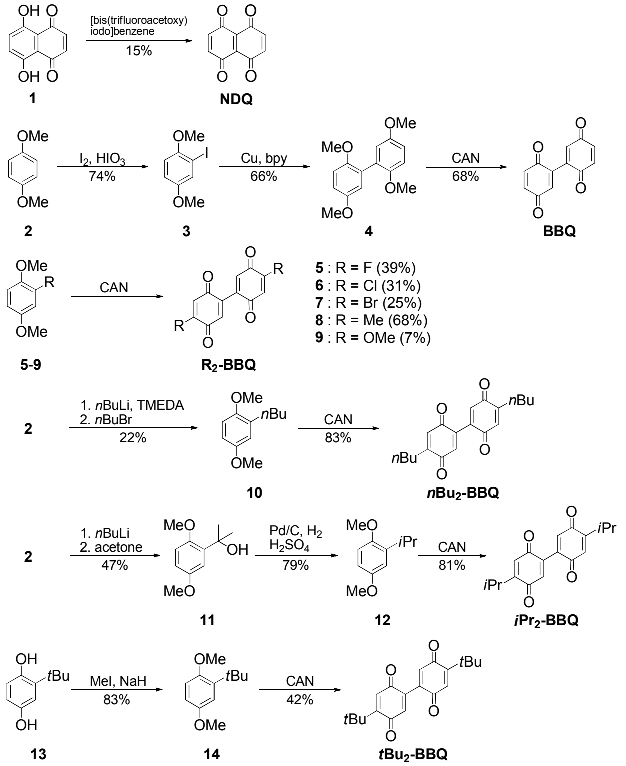
butylhydroquinone (**13**) through methylation of the hydroxyl groups in 83% yield[21] followed by CAN oxidation in 42% yield.[18]



Scheme 3 Synthetic pathways for the preparation of NDQ and BBQ derivatives.

Cyclic voltammetry

Cyclic voltammetry (CV) in the solution was applied to a 1.0 mM solution of samples in 0.1 M tetra-*n*-butylammonium perchlorate/acetonitrile (working electrode: glassy carbon (GC), counter electrode: platinum wire electrode, reference electrode: Ag/$AgNO_3$) system using an Automatic Polarization System (HSV-110, Hokuto Denko). The voltammogram was recorded at scan speed of 20 mV s^{-1} at room temperature. Potentials were corrected using ferrocene (Fc/Fc^+) as an internal standard. CV in the electrode was performed using the prepared cells as follows, and using a KIKUSUI PFX2011 computer-controlled automatic battery charge and discharge instrument. The electrode CV measurements were recorded at scan speed of 0.33 mV s^{-1} at 25°C in the cutoff voltage range of 1.5–4.2 V.

Preparation of coin cell and measurement of charge-discharge performance

Positive-electrode composites of coin-type cells containing 5 wt% positive-electrode materials fabricated with the composition: 5:85:10 wt% positive-electrode materials—vapour-grown carbon fibre (VGCF)—poly(tetrafluoroethylene) (PTFE). A positive disc 12 mm in diameter was made by pressing the composite followed by drying in vacuo. A porous polymer film separator was sandwiched between the positive disc and a Li metal plate, and the resulting material was placed in a coin-type cell with the electrolyte solution. The electrolyte solutions were a mixture of ethylene carbonate (EC; 30 vol%) and diethyl carbonate (DEC; 70 vol%) containing 1.0 M $LiPF_6$, ethyl isopropyl sulphone (EiPS) containing 1.0 M $LiN(SO_2CF_3)_2$ (LiTFSI), and tetraethylene glycol dimethyl ether (tetraglyme) containing 2.75 M LiTFSI.

The charge-discharge measurements of the cells were performed using a KIKUSUI PFX2011 computer-controlled automatic battery charge and discharge instrument. The measurements of the cells were performed at 25°C by the constant-current method at current densities of almost 40 mA g^{-1} in the cutoff voltage range of 1.5–4.2 V.

Results and Discussion

Comparison between charge–discharge performance of cells using BQ, NDQ, and BBQ as the cathode active materials in rechargeable batteries

The performance of the BQ-, NDQ-, and BBQ-based batteries was examined after preparing coin-type cells, using an electrolyte solution consisting of EC (30 vol%) and DEC (70 vol%) containing 1.0 M $LiPF_6$. Charge-discharge curves over eight cycles for the BBQ-based cells are exhibited in Fig. 3, whereas those for the BQ- and NDQ-based cells can be found in Fig. S1, in the ESI. In addition, the cycle-life performance over twenty cycles for the three cells is depicted in Fig. 4. The theoretical capacities for BQ (2 electrons), NDQ (4 electrons), and BBQ (4 electrons) are 496, 570, and 501 Ah kg^{-1}, respectively, whereas their observed initial capacities were 157, 347, and 326 Ah kg^{-1}, respectively. The practical capacities of the compounds are lower than the theoretical ones; the ratios of the first capacity to the theoretical values for BQ, NDQ, and BBQ were 32, 61, and 65%, respectively. The degradation might be caused by dissolution of the cathode active materials into the electrolyte solution before the charge-discharge tests. Solubility tests[22] revealed that NDQ and BBQ are less soluble in the EC/DEC solution than BQ, most likely because of their larger size.

The discharge voltages for the BQ-, NDQ-, and BBQ-based cells are 2.8, 1.8–3.4 (the first plateau: 3.4 V), and 2.9 V *versus* Li/Li^+, respectively. Several reports on organic cathode active materials[8e,11b,11c,11h] have revealed that cathode materials with lower lowest unoccupied molecular orbital (LUMO) energy levels (estimated via density functional theory (DFT) calculations) afforded higher discharge voltages. Furthermore, our recent report on BQ-based rechargeable batteries[12a] revealed that the first reduction peak ($E_{1p,c}$) in the cyclic voltammogram (CV) in solution corresponded to the discharge voltage, that is, cathode active materials with larger $E_{1p,c}$ produced higher discharge voltages. The calculated energy levels of the LUMOs for BQ, NDQ, and BBQ were –3.947, –4.645, and –4.251 eV, respectively (for details of the DFT calculations, see the ESI), and their measured $E_{1p,c}$ values in

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solution CV were –0.91, –0.34, and –0.76 V, respectively (Fig. 5, and Fig. S2 and Table S1 in the ESI). These results can be applied to the forementioned rule: namely, the expansion of the BQ skeleton is effective in improving the discharge voltage.

The BBQ-based cell demonstrated better cyclability compared to the BQ-based cell: the 20th discharge capacities for the BBQ- and BQ-based cells were 170 and 59 Ah kg^{-1}, respectively, and their ratios for the 20th capacity to the 1st were 52 and 37%, respectively. Although the NDQ-based cell also afforded a high initial capacity similar to the BBQ-based cell, the 20th discharge capacity for the cell was only 67 Ah kg^{-1}, and its ratio for the 20th capacity to the 1st was 19%, which is much less than the BBQ cell. Our recent paper utilizing alkylated BQs as cathode active materials[12b] revealed that the introduction of bulky substituents into the BQ skeleton significantly improved cyclability, which was based on the suppression of side reactions of the BQs in the cells. The anion radicals formed by redox reactions in the cells are quite reactive, and protection of the singly occupied molecular orbital (SOMO) of the anion radicals is important for suppressing side reactions. Bulky substituents on the BQ skeleton effectively prevent the approach of other molecules to the reactive SOMO of the anion radical. Accordingly, one BQ unit in BBQ would function as a protective group against the approach of other molecules to the SOMO of the other BQ unit. Indeed, as shown in Fig. 7, DFT calculations suggest that BBQ has a twisted geometry in which the dihedral angle between the two BQ planes is predicted to be 41°. Comparison of the performance of the three quinonoid compounds (BQ, BBQ, and NDQ) reveals that BBQ would be superior for a rechargeable battery application; thus, we have focused on BBQ and its derivatives in the following discussion.

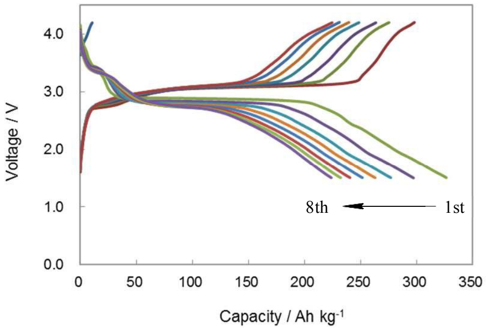

Fig. 3 Charge-discharge curves and cycle-life performance over eight cycles for BBQ cell in 1.0 M LiPF$_6$-EC/DEC.

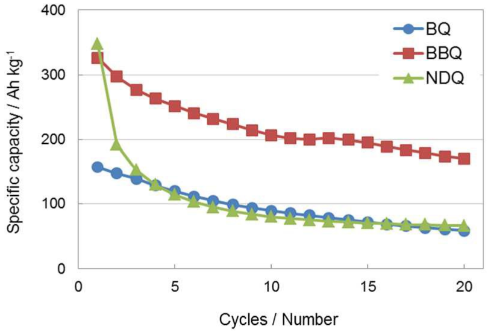

Fig. 4 Cycle-life performance over twenty cycles for cells based on BQ, NDQ, and BBQ.

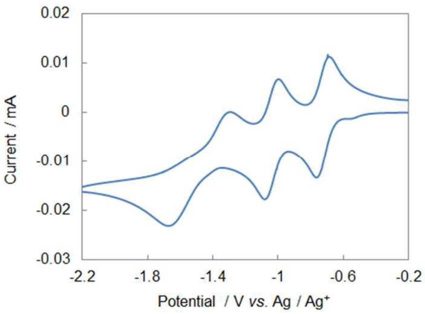

Fig. 5 CV of BBQ in acetonitrile.

Number of acceptable electrons for BBQ derivatives

The observed initial capacity of BBQ (326 Ah kg^{-1}) is far from the theoretical value based on four electrons (501 Ah kg^{-1}), but close to that based on three electrons (376 Ah kg^{-1}). Two-electron redox reactions generally occur in BQ derivatives. Interestingly, in the case of BBQ derivatives, the data suggest that three- rather than four-electron redox reactions may occur. This phenomenon was also observed in the solution CV of BBQ (Fig. 5), in which three pairs of redox peaks were observed, with each pair corresponding to a one-electron redox reaction. The energy differences (ΔE) for the redox reactions of BQ and BBQ were estimated by DFT calculations and are illustrated in Fig. 6.[23,24] Neutral BQ accepts an electron to afford an anion radical with a stabilization of –208.8 kJ mol^{-1} (ΔE_1). The anion radical accepts another electron to generate a dianion with a destabilization of 313.4 kJ mol^{-1} (ΔE_2); the dianion is unstable compared to the neutral BQ. Not unexpectedly, the radical trianion is extremely unstable compared to the dianion (ΔE_3 = 747.6 kJ mol^{-1}), as BQ derivatives cannot accept three electrons. Analogously, neutral BBQ receives an electron to generate an anion radical with a stabilization of –273.7 kJ mol^{-1} (ΔE_1), which indicates that BBQ is more stabilized by the acceptance of one electron compared to BQ. The BBQ anion radical can be stabilized by resonance, which is supported by the calculated length of the C–C bond connecting the two rings in BBQ (1.478 and 1.467 Å in the neutral and anion radical forms, respectively, Fig. 7). The shortening of the C–C bond indicates its increasing double-bond character by resonance. The resonance effect is also supported by the radical densities of the oxygen atoms; the

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calculated spin density of the oxygen atoms in the BQ anion radical was 0.261, whereas those in BBQ were predicted to be 0.180 and 0.077. Thus, the spin densities in BBQ are relatively delocalized. Although the dianion formed by the acceptance of another electron results in destabilization by 94.7 kJ mol^{-1} (ΔE_2), it is still more stable than the neutral BBQ. The dianion receives an electron to afford radical trianions with a destabilization of 512.4 kJ mol^{-1} (ΔE_3), and in this reductive step, BBQ becomes unstable compared to the neutral BBQ for the first time. Although the radical trianion can accept another electron to form a tetraanion, a considerable energy change of 831.8 kJ mol^{-1} (ΔE_4) is predicted. Since significant destabilization is unavoidable in forming the BBQ tetraanion, the calculations confirm that BBQ can accept not four but three electrons.

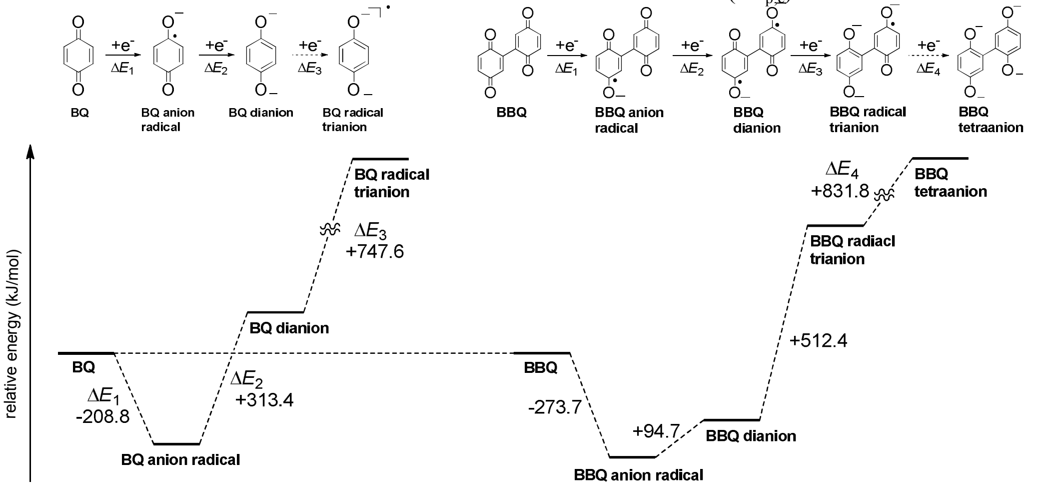

Fig. 6 Energy profiles of BQ and BBQ for redox reactions at the B3LYP/6-31+G* level.

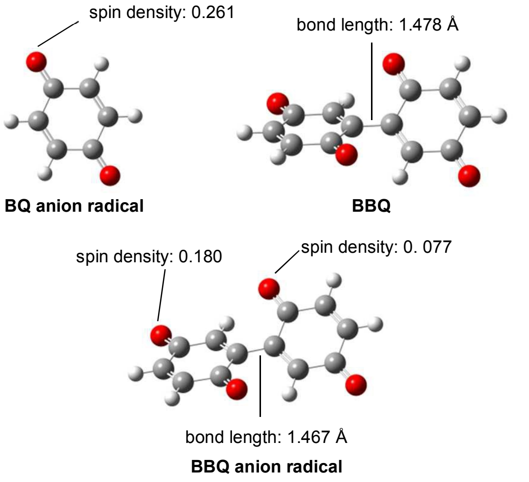

Fig. 7 Optimized structures of BQ anion radical, BBQ, and BBQ anion radical. Geometries were optimized at the B3LYP/6-31+G* level.

Cyclic voltammetry of electrodes using BBQ

Based on the solution CV of BBQ (Fig. 5), discharge curves with three phases should be observed in the charge-discharge test; however, a single plateau at 2.9 V was observed in the practical discharge curve in the initial cycle, as shown in Fig. 3. To clarify the redox behaviour in the electrode, the electrode CV for the BBQ cell (1.0 M $LiPF_6$-EC/DEC) at the initial cycle was measured and is depicted in Fig. 8. The figure shows a reduction peak of 2.58 V, which corresponds to the single plateau in the charge-discharge test. We previously reported that the difference ($\Delta E_{p,c}$) between the first reduction peak potential ($E_{1p,c}$) and the second ($E_{2p,c}$) in the electrode CV was lower than that in the solution CV.[12a] For instance, the $\Delta E_{p,c}$ in the electrode CV involving CF_3-BQ was 0.16 V, whereas that in its solution CV was 0.82 V.[25] Since this potential shift is likely caused by the coordination of Li^+ to the oxygen atom(s) of the CF_3-BQ during the redox reaction in the electrode,[11i] the shift should also occur in BBQ derivatives. For the solution CV of BBQ, $E_{1p,c}$, $E_{2p,c}$, and $E_{3p,c}$ were observed at –0.76, –1.08, and –1.67 V, respectively, as shown in Fig. 5. Considering the potential shift, the first and second reduction peaks in the electrode CV would certainly overlap to afford a single reduction peak. Consequently, it would not be surprising if the combined reduction peak and the third reduction peak also overlapped to afford a pseudo-single reduction peak, because the difference between $E_{1p,c}$ and $E_{2p,c}$ is quite low, and $E_{3p,c}$ is also close. The reduction peak at 2.58 V in the electrode CV is of higher current intensity compared to the oxidation peaks at 2.86 and 3.27 V, indicating that the reduction peak results from the overlap of some peaks. Additionally, the electrode CVs for the Me_2- and Br_2-BBQ cells (1.0 M $LiPF_6$-EC/DEC) at the initial cycle were measured and are depicted in Fig. S3 in the ESI. Although the CV of the BBQ cell shows a single reduction peak, those of the Me_2- and Br_2-BBQ cells reveal two partially overlapped redox peaks with different intensities. These results suggest that the reduction peak in the CV for the BBQ cell

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would be formed by the overlapping of three reduction peaks, and BBQ derivatives would accept three electrons. Similarly, a potential shift was confirmed for the oxidation peaks; in the solution CV, the first oxidation peak of –0.69 V is close to the second oxidation peak of –1.01 V, and thus, in the electrode, both peaks should combine to afford a pseudo-single oxidation peak which would partially overlap with the third oxidation peak. Based on the above discussion and the fact that, in the electrode CV, the oxidation peak at 2.86 is of lower current intensity compared to that at 3.27 V, the oxidation peaks at 2.86 and 3.27 V should correspond to the one- and two-electron oxidation reactions, respectively. Finally, the electrode CVs of the 1st to the 8th cycles, presented in Fig. S4 in the ESI, showed no change in peak shape from the 1st to the 8th cycle, indicating that the capacity degradation during cycling is not caused by decomposition of the BBQ.

Table 1 Electrochemical parameters for cells based on BBQ derivatives.

Sample	$E_{1p,\,c}$ in solution CV (V)	Discharge voltage of 1st cycle (V)	Theoretical capacity (Ah kg^{-1}) 3 electrons / 4 electrons	Practical capacity (Ah kg^{-1}) 1st cycle	2nd	20th	Capacity retention^{a} (%)
BBQ	-0.76	2.8	375 / 501	358	368	239	67
F_2-BBQ	-0.60	2.7	322 / 429	333	134	39	12
Cl_2-BBQ	-0.58	2.8	284 / 379	276	299	187	68
Br_2-BBQ	-0.58	2.9	216 / 288	252	202	283	>99^{b}
Me_2-BBQ	-0.86	2.6	332 / 443	302	293	138	46
nBu_2-BBQ	-0.85	2.7	246 / 328	281	252	103	37
iPr_2-BBQ	-0.86	2.7	269 / 359	284	270	126	45
tBu_2-BBQ	-0.86	2.6	246 / 328	286	268	127	45
$(OMe)_2$-BBQ	-0.84	2.7	293 / 391	382	323	229	60

^{a} Ratio of the 20th capacity to the 1st cycle. ^{b} The capacity was rapidly decreased at around 25th cycle.

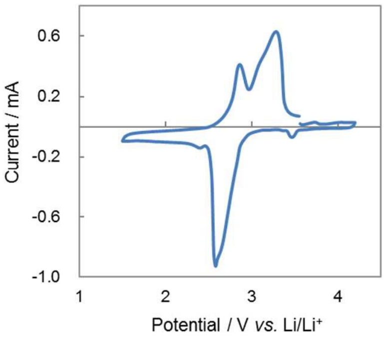

Fig. 8 Electrode CV of BBQ cells (1.0 M $LiPF_6$-EC/DEC) at initial cycle.

Charge-discharge performance of cells using BBQ derivatives as cathode active materials in rechargeable batteries

Next, to examine the substituent effects of BBQ derivatives on battery performance, we prepared coin-type cells containing R_2-BBQ (R = F, Cl, Br, Me, *n*Bu, *i*Pr, *t*Bu, OMe) as cathode active materials. Tetraglyme containing 2.75 M LiTFSI was employed as the electrolyte solution, since the BBQ cell in the tetraglyme system exhibited relatively high cycle retention. For details of the examination of electrolyte effects, see the ESI. The cycle-life performance over twenty cycles for the F_2-, Cl_2-, *t*Bu_2-, and $(OMe)_2$-BBQ cells is exhibited in Fig. 9, and that for the other cells can be found in Fig. S5 in the ESI. The battery performance results are also summarized in Table 1. Charge-discharge curves and cycle-life performance over eight cycles for the cells can be found in Fig. S6 in the ESI. The initial discharge capacities for the F_2-, Cl_2-, and Br_2-BBQ cells were 333, 276, and 252 Ah kg^{-1}, respectively, which do not reach the theoretical values based on four electrons (429, 379, and 288 Ah kg^{-1}, respectively), but approximate those for three electrons (322, 284, and 216 Ah kg^{-1}, respectively). Although the Br_2-BBQ cell provided the highest cycle retention (ratio of the 20th capacity to the 1st cycle: >99%) in the halogenated BBQ (F_2-, Cl_2, and Br_2-BBQ) cells, rapid capacity degradation was observed near the 25th cycle.[26] The F_2-BBQ cell afforded a considerably poor capacity retention (ratio of the 20th capacity to the 1st cycle: 12%) caused by the remarkable capacity fading between the 1st and 2nd cycles. In fact, although the 2nd discharge capacities for Cl_2- and Br_2-BBQ cells (299 and 202 Ah kg^{-1} respectively) are close to their theoretical values involving three electrons, that for the F_2-BBQ cell (134 Ah kg^{-1}) is much lower than its theoretical value. The solubilities of BBQ derivatives in electrolyte solution were measured (see the ESI for details), and F_2-BBQ exhibited the highest solubility in the halogenated BBQs. Its high solubility might cause the remarkable capacity degradation of the corresponding cell. However, the order of the capacity retention of halogenated BBQ-based cells does not correspond to their solubility order. In addition, whereas BBQ exhibited higher solubility than $(OMe)_2$-BBQ, the BBQ-based cell provided higher capacity retention than the $(OMe)_2$-BBQ-based cell. The poor correlation between the solubility of BBQ derivatives and capacity retention of the corresponding cells indicates that capacity retention for the cells is determined by the solubility as well as other factors. Namely, the stability of the BBQ derivatives during cycling and the solubility of their reduced species may also influence the cells' capacity retention. However, it is quite difficult to elucidate these effects at present, and the details are under investigation.

The discharge voltages of the halogenated BBQ cells were 2.7–2.9 V, which are higher than those of the alkylated BBQ (Me_2-, *n*Bu_2-, *i*Pr_2-, and *t*Bu_2-BBQ) and $(OMe)_2$-BBQ cells (2.6–2.7 V). The differences in the discharge voltages can be rationalized by their redox potentials. Indeed, the electron-rich

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alkylated BBQ and $(OMe)_2$-BBQ afforded relatively low $E_{1p,c}$ values in the solution CVs (about –0.85 V), whereas the halogenated BBQs are electron-deficient because of the electronegativity of halogen atoms and exhibited high $E_{1p,c}$ values (about –0.59 V). Positive shifts due to the introduction of halogens in the BBQ skeleton were also observed in other redox peak potentials in the solution CVs (Fig. S7 in the ESI). These results revealed that the introduction of electron-withdrawing groups into the BBQ skeleton raises the redox potential, and therefore improves the discharge voltages for the cell.

The cells based on alkylated BBQs exhibited similar capacity retentions (37–46%) that are lower than that of BBQ (67%). The first discharge capacities for Me_2-, *n*Bu_2-, *i*Pr_2-, and *t*Bu_2-BBQ cells (302, 281, 284, and 286 Ah kg^{-1}, respectively) are similar to their theoretical values involving three electrons (332, 246, 269, and 246 Ah kg^{-1}, respectively) rather than four electrons (443, 328, 359, and 328 Ah kg^{-1}, respectively), and their second discharge capacities (293, 252, 270, and 268 Ah kg^{-1}, respectively) approximate those involving three electrons. These results indicate that BBQ derivatives would work not as four-, but rather, as three-electron acceptors. Interestingly, the initial discharge capacity for the $(OMe)_2$-BBQ cell was 382 Ah kg^{-1}, which corresponds well to the theoretical value involving four electrons (391 Ah kg^{-1}). Even in the second cycle, the discharge capacity (323 Ah kg^{-1}) still exceeds the theoretical value involving three electrons (293 Ah kg^{-1}).

To further confirm that the $(OMe)_2$-BBQ accepts four electrons, its CVs in solution (tetra-*n*-butylammonium perchlorate/acetonitrile) and electrode were measured. As shown in Fig. S7h in the ESI, the CV in acetonitrile displayed three pairs of redox peaks, similar to that for BBQ. However, the CV in the electrode for $(OMe)_2$-BBQ revealed two slightly overlapped reduction peaks at 1.94 and 2.52 V and a broad oxidation peak at 3.03 V (Fig. S8), which obviously differ from those for Br_2- and Me_2-BBQ (Fig. S3 in ESI). The CVs of Br_2- and Me_2-BBQ in the electrode indicate that the current intensity of the first reduction peak is nearly twice that of the second reduction peak, whereas the CV of the electrode involving $(OMe)_2$-BBQ shows that the current intensities of the first and second reduction peaks are nearly the same. These observations suggest that each of the reduction peaks for $(OMe)_2$-BBQ corresponds to a two-electron reduction, whereas the two reduction peaks for Br_2- and Me_2-BBQ correspond to one- and two-electron reduction steps, respectively. Therefore, we conclude that in the electrodes, BBQ derivatives generally act as three-electron acceptors, except for $(OMe)_2$-BBQ, which accepts four electrons. Although the reason that $(OMe)_2$-BBQ accepts four electrons in the electrode is unclear, counter cations (nBu_4N^+ or Li^+) may play a significant role in determining the number of electrons accepted by $(OMe)_2$-BBQ.

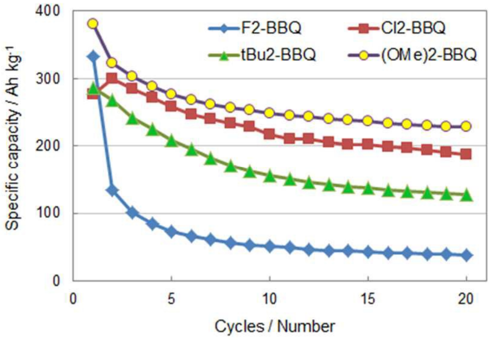
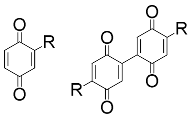


Fig. 9 Cycle-life performance over twenty cycles for cells based on R_2-BBQ (R = F, Cl, *t*Bu, and OMe) in 2.75 M LiTFSI-tetraglyme systems.

Comparison of battery performance between R_2-BBQ and the dimer of R-BQ

To clarify the effects of dimerizing the BQs on battery performance, cells using R-BQ (R = Cl, Me, OMe), the monomers of R_2-BBQ, as positive electrode active materials were prepared, and their charge-discharge performance was assessed. Tetraglyme containing 2.75 M LiTFSI was used as the electrolyte solution for the cells. The cycle-life performance of Me-BQ and Me_2-BBQ cells is shown in Fig. 10, and that of the other R-BQ and R_2-BBQ cells can be found in Fig. S9 in the ESI. The charge-discharge curves over eight cycles for the R-BQ cells are available in Fig. S10 in the ESI. The theoretical capacities of the R-BQ (R = Cl, Me, OMe) cells were 376, 439, and 388 Ah kg^{-1}, respectively, which are nearly the same as those of the corresponding R_2-BBQ (R = Cl, Me, OMe) cells involving four electrons. However, the R-BQ cells afforded much smaller practical capacities than their theoretical ones. Indeed, the initial capacities of the R-BQ (R = Cl, Me, OMe) cells were 171, 63, and 199 Ah kg^{-1}, respectively, whereas those of the R_2-BBQ (R = Cl, Me, OMe) cells were 276, 302, and 382 Ah kg^{-1}, respectively (Table 1). As discussed earlier,[22] the solubility of the R_2-BBQs in the electrolyte solution would be much lower than those of the R-BQs. Accordingly, the R-BQ cells would suffer significantly decreased initial capacities because of active material dissolution, while the R_2-BBQ cells would be able to maintain their capacities at near-theoretical values. These outcomes prove that the dimerization of BQs is an effective strategy for improving battery performance, especially the initial capacity.



R-BQ **R_2-BBQ**
(R = Cl, Me, OMe)

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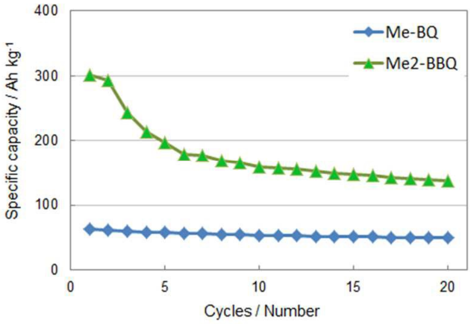

Fig. 10 Cycle-life performance over twenty cycles for cells based on Me-BQ and Me_2-BBQ in 2.75 M LiTFSI-tetraglyme systems.

Cycle-life performance of BBQ and $(OMe)_2$-BBQ cells over 50 cycles

An examination of the substituent effects of BBQ derivatives on battery performance reveals that the cells based on halogenated BBQ derivatives exhibited relatively high voltages but low capacities and capacity retentions. Meanwhile, the cells involving alkyl groups in BBQ skeleton afforded lower voltages, capacities, and capacity retentions, indicating that these substituent groups do not improve battery performance. On the other hand, the non-substituent BBQ and $(OMe)_2$-BBQ cells provided excellent charge-discharge performance over 20 cycles. Their extended cycle-life performance over 50 cycles was examined. The results for the BBQ cell are depicted in Fig. 11, whereas those for the $(OMe)_2$-BBQ cell can be found in Fig. S11 in the ESI. Both cells exhibited significant decreases in discharge capacities during the first few cycles, but thereafter, the capacity degradation was less rapid. The 50th discharge capacities for the BBQ and $(OMe)_2$-BBQ cells were 198 and 189 Ah kg^{-1}, respectively, and cycle retention rates at the 50th cycle were 55 and 50%, respectively. In addition, their Coulombic efficiencies both remained above 95% over 50 cycles, except for the first few cycles. As far as we know, among batteries that use low-molecular-weight organic compounds as cathode active materials with a standard battery system, the performance for the BBQ battery cell is much better than any other cell reported previously.

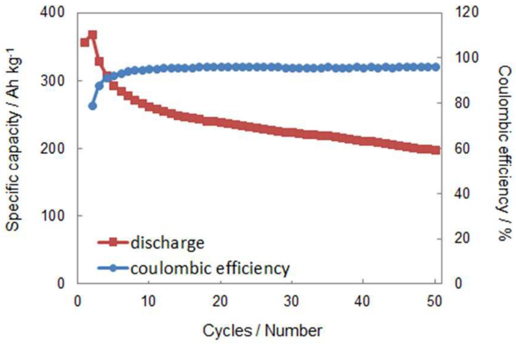

Fig. 11 Cycle-life performance over 50th cycles for cells based on BBQ in 2.75 M LiTFSI-tetraglyme systems.

Conclusions

In conclusion, we prepared NDQ and BBQ derivatives and utilized them as cathode active materials in rechargeable lithium batteries for the first time. The cells using BBQ derivatives performed significantly better compared to those using BQ derivatives. For example, the BQ-based cell afforded a discharge voltage of 2.8 V, an initial capacity of 157 Ah kg^{-1}, and a 20th discharge capacity of 59 Ah kg^{-1}, whereas the BBQ-based cell produced a discharge voltage of 2.9 V, an initial capacity of 326 Ah kg^{-1}, and a 20th discharge capacity of 170 Ah kg^{-1}. The BBQ derivatives were expected to work as four-electron acceptors since BBQ is a dimer of BQ with four carbonyl groups. However, it was discovered that they generally act as three-electron acceptors, which was verified by the practical cell capacities, CV measurements, and DFT calculations. On the other hand, the introduction of methoxy groups into the BBQ skeleton increased the number of electrons accepted; the initial discharge capacity for the $(OMe)_2$-BBQ cell was 382 Ah kg^{-1}, which closely corresponds to the theoretical value involving four electrons (391 Ah kg^{-1}). Extended cycle measurements over 50 cycles for the BBQ cell also revealed a high cycle retention of 55% (50th capacity: 198 Ah kg^{-1}); these cyclability and capacity values are remarkably high for a low-molecular-weight organic cathode active material. These results reveal that BQ dimerization is an effective strategy for improving battery performance.

Importantly, although low-molecular-weight organic cathode active materials have been discounted among LIB researchers due to their poor cycle-life performance, organic compounds have great potential as next-generation cathode active materials with much higher capacities. By continuing to use inorganic compounds as cathode active materials, dramatic improvements in battery performance will be difficult because of their limited theoretical capacities, since the inorganic materials generally undergo single-electron redox reactions. In contrast, batteries using organic cathode active materials should produce significant battery performance improvements.

The battery performance of cells using low-molecular-weight organic cathode active materials should be sensitive to cell configurations; the optimization of battery materials such as the electrolyte, solvent, separator, and binder should remarkably improve battery performance because these materials have been exclusively used for inorganic batteries and have never been optimized for organic batteries. Therefore, although organic-based batteries have great potential for future practical use, to achieve a major breakthrough in organic secondary batteries, the development of appropriate battery systems for organic cathode active materials is required, in addition to the synthesis of the high-performance organic cathode materials themselves.

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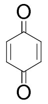
22 Identical amounts of BQ, NDQ, and BBQ (4.5 mg) were added to individual EC/DEC solutions (0.5 mL), and the mixtures were stirred at 25 °C for 5 min. Whereas the BQ was completely dissolved in the solution, some of the NDQ and BBQ did not dissolve.
23 A detailed study of the redox mechanisms for a cell based on quinone-type cathode active materials had been reported (A. L. M. Reddy, S. Nagarajan, P. Chumyim, S. R. Gowda, P. Pradhan, S. R. Jadhav, M. Dubey, G. John and P. M. Ajayan, *Sci. Rep.*, 2012, **2**, 960), in which the lithiated products were characterized by spectroscopic methods such as NMR. The paper indicated that a redox reaction involving Li^+ insertion/extraction reactions occurs in quinone-based cells. In our DFT calculations, Li^+ was omitted for simplicity.
24 Reduced species of BQ and BBQ can form multi-spin states. These were all calculated, and the most stable spin states are employed in the discussion. For details, see the ESI.
25 $\Delta E_{p,c}$ values for CH_3-BQ in the electrode CV and in the solution CV were 0.25 and 0.71 V, respectively, whereas those for C_4F_9-BQ were 0.30 and 0.95 V, respectively, suggesting that the potential shift should occur for every BQ derivative.
26 To examine the reproducibility of the cyclability for the Br_2-BBQ-based cell, cycle tests using freshly prepared coin cells were carried out; cycle-life performance very similar to those in Fig. S5 in the ESI was observed. Furthermore, the effect of the electrolyte in the Br_2-BBQ cell was examined by preparing cells containing EiPS with 1.0 M LiTFSI or a mixture of EC (30 vol%) and DEC (70 vol%) with 1.0 M $LiPF_6$. Similarly, rapid capacity degradation was observed over cycles 15–20 (Fig. S12, ESI).

Table of Contents

Compounds based on 2,2′-bis-*p*-benzoquione framework as cathode active materials improved the performance of rechargeable batteries, revealing that the BBQ-based cells exhibited excellent performance, compared to benzoquinone monomers.



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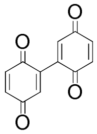

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