

Steric Effects on the Cyclability of Benzoquinone-type Organic Cathode Active Materials for Rechargeable Batteries

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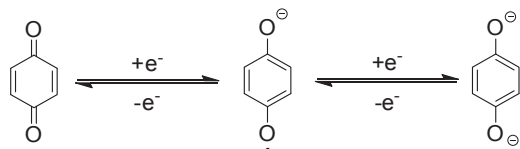
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Benzoquinone derivatives, which undergo reversible two-electron redox reactions, should afford high capacity as positive electrode materials for rechargeable batteries. Although some benzoquinones have been reported as cathode active materials, their low cycle-life performance is a drawback. We prepared benzoquinones bearing alkyl groups with various degrees of bulkiness to investigate the relationship between the steric effects of the substituents on the benzoquinone skeleton and the battery performance. The introduction of bulky substituents, especially a *tert*-butyl group, on the skeleton significantly improved the cyclability.

Rechargeable lithium-ion batteries (LIBs) that use LiCoO₂ as the cathode active material are widely utilized as energy sources for various electrical devices.¹ However, there is an urgent need to improve the mass energy density of the batteries to extend their use to high-energy-consuming devices such as electric vehicles.² Organic positive electrode materials should produce higher mass energy densities than inorganic ones, because the latter generally act as only one-electron acceptors, whereas organic materials can often accept two or more electrons and thereby afford higher capacities. Furthermore, they could surmount the safety and material resource availability issues of the classical battery using LiCoO₂.

Various types of organic cathode active materials have been reported as effective substitutes for classical inorganic ones.^{3,4} Benzoquinone derivatives (BQs) fall into the carbonyl class of cathode active materials, and afford reversible redox reactions involving two electrons (Scheme 1).⁵ Although they provide high capacities because of their low-molecular-weight skeletons, low discharge voltages, and inadequate cycle-life performance are drawbacks of BQ-type cathode active materials. Moreover, the relationship between the structures of the cathode active materials and their performance is not well understood, which complicates the research and design of new candidates. Therefore, we recently attempted to determine the relationship between the structure of a BQ-type cathode active material and its discharge voltage, and revealed that the electronic effects of substituents on the BQ skeleton affect discharge voltages; indeed, electron-deficient BQs afforded high discharge



Scheme 1. Reversible redox reactions involving two electrons in BQs.

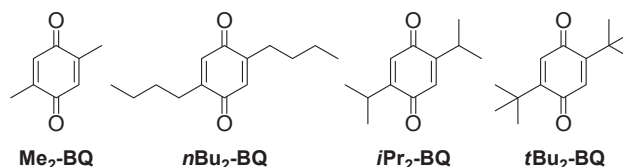


Figure 1. Structures of BQs bearing alkyl groups with various degrees of bulkiness (Me, *n*Bu, *i*Pr, and *t*Bu) for utilization as cathode active materials in rechargeable LIBs.

voltages.^{5c} However, methods to improve the cycle-life performance remain to be investigated. Such a clarification is extremely important because the cyclability of cells using low-molecular-weight organic cathode materials is lower than that of inorganic-based cells. Herein, we report the steric effects of the introduced substituents on the battery and cycle-life performance; BQs bearing functional groups with different steric bulks were prepared and incorporated into cells for battery performance evaluations (Figure 1). It should be noted that an approach that utilizes the structural diversity of organic compounds has never been reported for the improvement of cycle-life performance in BQ-based cells, apart from the development of new battery systems.⁶

2,5-Dibutyl-1,4-benzoquinone (*n*Bu₂-BQ)⁷ and 2,5-diisopropyl-1,4-benzoquinone (*i*Pr₂-BQ)⁸ were synthesized according to the procedure outlined in Scheme S1 (for details of the synthesis, see the Supporting Information). The other BQs were purchased and used without further purification.

Positive-electrode composites of coin-type cells containing almost 10 wt % positive electrode materials were fabricated with the composition 10:80:10 wt % positive electrode materials–vapor-grown carbon fiber (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 solution was tetraethylene glycol dimethyl ether (tetraglyme) containing 2.75 M LiN(SO₂CF₃)₂ (LiTFSI). The charge–discharge measurements of the cell were performed at 25 °C by the constant-current method at 0.1 mA in the cutoff voltage range of 1.5–4.2 V and at a current density of around 50 mA g⁻¹.

The charge–discharge curves and cycle-life performance of R₂-BQ (R = Me, *i*Pr, and *t*Bu) over eight cycles are shown in Figure 2, while their cycle-life performance over fifteen cycles is exhibited in Figure 3; their battery performance is summarized in Table 1.⁹ The cell based on Me₂-BQ afforded a first discharge capacity, 226 A h kg⁻¹, which was significantly lower than the theoretical value, 394 A h kg⁻¹, and its cyclability

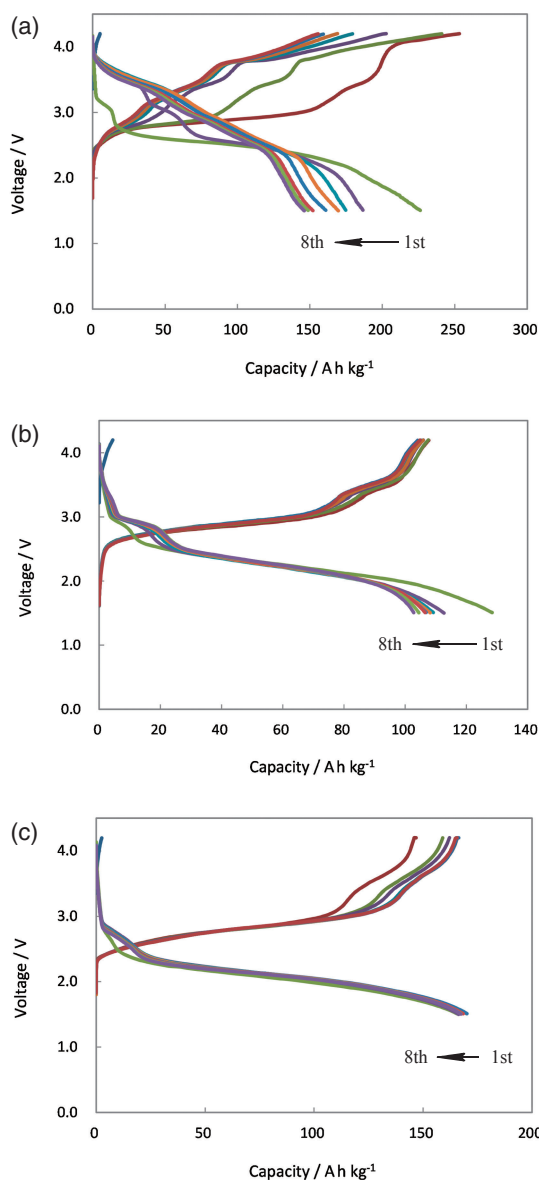


Figure 2. Charge–discharge curves and cycle-life performance over eight cycles for cells based on (a) $\text{Me}_2\text{-BQ}$, (b) $i\text{Pr}_2\text{-BQ}$, and (c) $t\text{Bu}_2\text{-BQ}$.

Table 1. Battery performance of $\text{R}_2\text{-BQ}$ cells

Sample	Discharge voltage/V	Theoretical capacity/ A h kg^{-1}	Practical capacity/ A h kg^{-1}		
			1st cycle	2nd	15th
$\text{Me}_2\text{-BQ}$	2.5	394	226	187	129 (57%) ^a
$i\text{Pr}_2\text{-BQ}$	2.2	279	128	113	94 (73)
$t\text{Bu}_2\text{-BQ}$	2.0	243	165	166	158 (96)

^aRatio of the capacity to the 1st cycle.

was poor, as represented in the ratio of the 15th discharge capacity (129 A h kg^{-1}) to the 1st of 57%. However, the $i\text{Pr}_2\text{-BQ}$ and $t\text{Bu}_2\text{-BQ}$ cells showed high cycle retention; the ratios of the 15th discharge capacity to the 1st were 73% (capacity of the 1st cycle: 128 A h kg^{-1} , and that of the 15th cycle: 94 A h kg^{-1}) and 96% (capacity of the 1st cycle: 165 A h kg^{-1} , and that of the 15th cycle: 158 A h kg^{-1}), respectively. As far as we know, the $t\text{Bu}_2\text{-$

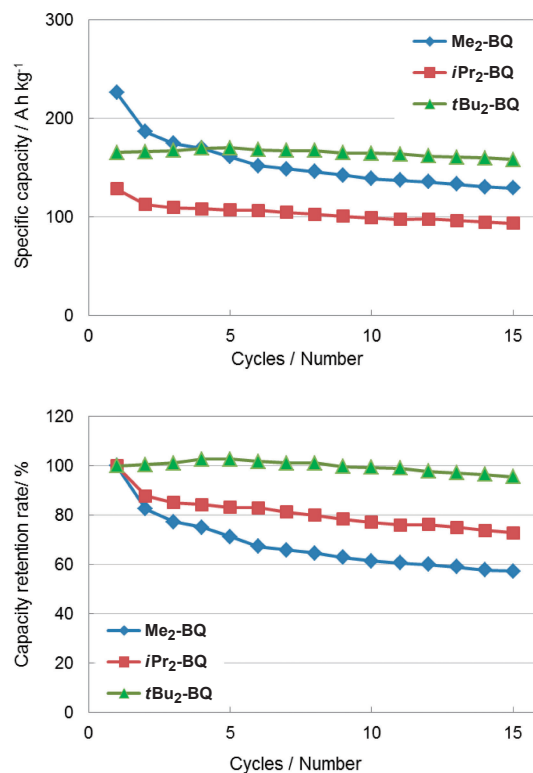


Figure 3. Cycle-life performance over fifteen cycles for cells based on $\text{Me}_2\text{-BQ}$, $i\text{Pr}_2\text{-BQ}$, and $t\text{Bu}_2\text{-BQ}$: plots of specific capacity versus cycle number, and the capacity retention rate versus cycle number.

BQ -based cell provided the highest cyclability among the BQ -based cathode active materials for a standard rechargeable LIB system. The order of cyclability is $t\text{Bu}_2\text{-BQ} > i\text{Pr}_2\text{-BQ} > \text{Me}_2\text{-BQ}$, which correlates with the steric bulk. These results indicated that the introduction of bulky functional groups improves cyclability in BQ -based cells.

Additionally, the effects of the 1.0 M LiTFSI-ethyl isopropyl sulfone (EiPS) and 1.0 M LiPF_6 -ethylene carbonate (EC)/diethyl carbonate (DEC) (30:70 v/v) electrolyte systems using $\text{R}_2\text{-BQ}$ -based cells were examined; their cycle-life performance can be found in the Supporting Information, Figures S2 and S3. For the $i\text{Pr}_2\text{-BQ}$ cells, the ratio of the 15th discharge capacity to the 1st was 30% in the EC/DEC system and 54% in the EiPS system, both of which were inferior to that in the tetraglyme system, 73%. A similar trend in the cyclability was observed in the $t\text{Bu}_2\text{-BQ}$ -based cell; the ratios of the 15th discharge capacity to the 1st were nearly 0% in the EC/DEC system, and 45% in the EiPS system, versus 96% in the tetraglyme system. These results indicate that the tetraglyme system affords the most stable cyclability for the BQ -based cells among the three electrolyte systems employed.

Based on the cyclic voltammograms of the $\text{R}_2\text{-BQs}$, in which two pairs of redox peaks were observed (Figure S4), the charge–discharge mechanism for the BQ derivatives in the cells should involve stepwise redox reactions involving two electrons, as shown in Scheme 1. The capacity fade during charge–discharge cycling would be mainly ascribed to side reactions in the cells; the instability of the formed anion radical might be a

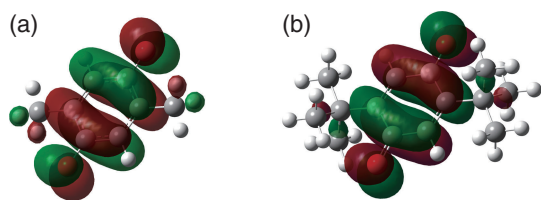


Figure 4. Optimized structures and SOMOs of the anion radical for (a) Me₂-BQ and (b) *t*Bu₂-BQ. Atom colors: C, grey; H, white; O, red. Geometry optimization were performed at the B3LYP/6-31+G* level.

major cause of these reactions. To clarify the steric effects of substituents on the cyclability, we calculated the singly occupied molecular orbitals (SOMOs) in the anion-radical states for Me₂-BQ and *t*Bu₂-BQ via density functional theory (DFT). The optimized Kohn–Sham orbitals of the SOMOs are depicted in Figure 4. The SOMOs are delocalized on the BQ skeleton, and other molecules would need to approach the SOMO for side reactions to occur. Protecting the SOMOs would prevent the approach of other molecules and thus improve cycle-life performance; that is, bulky functional groups introduced into the BQ skeleton can effectively shield the reactive radical (SOMO). Comparing the two molecules, it is visually clear that the SOMO of *t*Bu₂-BQ is effectively protected by its substituents. Additionally, the neutral and dianion species of Me₂-BQ and *t*Bu₂-BQ were calculated and the energy differences (ΔE) for the redox reactions were estimated.¹⁰ The results implied that the ΔE value between the neutral and anion radical species of *t*Bu₂-BQ ($-197.1 \text{ kJ mol}^{-1}$) was similar to that of Me₂-BQ ($-189.5 \text{ kJ mol}^{-1}$), whereas the ΔE value between the anion radical and dianion species of *t*Bu₂-BQ ($269.6 \text{ kJ mol}^{-1}$) was significantly lower than that of Me₂-BQ ($306.5 \text{ kJ mol}^{-1}$). Thus, the capacity fading during cycling might be related to not only the steric effects in the anion radical, but also the stability of the dianion species. These help explain the results for the R₂-BQ cells, in which the cyclability order corresponded to the size of the alkyl groups (*t*Bu > *i*Pr > Me).

In conclusion, we prepared BQ derivatives bearing sterically graduated alkyl groups for use as cathode active materials in rechargeable LIBs. The *t*Bu₂-BQ cells showed much higher cycle retention rates than the other R₂-BQ cells; the ratio of the 15th capacity to the 1st was 96% in the *t*Bu₂-BQ cell, which is better by far than that of any BQ-based cell reported previously. These results indicate that the introduction of bulky functional groups into the BQ skeleton is effective in improving the cycle-life performance. DFT calculations revealed that the bulky BQ substituents effectively protect the reactive BQ anion radical and suppress side reactions during the charge–discharge cycles.

In the research area of organic cathode active materials for LIBs, the molecular design of potential materials is complicated by the lack of information about the relationship between molecular structure and battery performance. Therefore, studies on organic cathode active materials are quite rudimentary and have not reached the mature developmental stage of the inorganic analogues. In this paper, we revealed the relationship between the cyclability and structure of the cathode active materials in BQ-based cells for rechargeable LIBs, which will be significant toward the development of high-performance organic rechargeable batteries in the future.

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Supporting Information is available electronically on J-STAGE.

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- The initial and second capacities of the *n*Bu₂-BQ cell exceeded the theoretical value, indicating that the redox reaction in the electrode might be different from those of the other R₂-BQ cells. See the Supporting Information, Figure S1.
- For details, see the Supporting Information, Figure S5.