

Available online at www.sciencedirect.com**SciVerse ScienceDirect**

Energy Procedia 34 (2013) 880 – 887

Energy
Procedia

10th Eco-Energy and Materials Science and Engineering
(EMSES2012)

Dialkoxybenzoquinone-type active materials for rechargeable lithium batteries: the effect of the alkoxy group length on the cycle-stability

Masaru Yao*, Hisanori Ando, Tetsu Kiyobayashi

*Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*

Abstract

The performance of 2,5-di-*n*-decyloxy-1,4-benzoquinone (DDBQ) as an active material for rechargeable lithium batteries was investigated. The prepared electrode in which DDBQ was incorporated showed an initial discharge capacity of 125 mAh/g_(DDBQ) with an average voltage of 2.5 V vs. Li⁺/Li. The obtained discharge capacity corresponds to a benzoquinone-based two-electron redox behavior. In the cycle-life test, the prepared DDBQ-electrode showed a relatively good performance; it maintained about 60% of the initial capacity after 20 cycles. The observed cycle-stability was compared to those of the other dialkoxybenzoquinones bearing shorter alkoxy chains, such as the methoxy, ethoxy, and propoxy groups. The correlation between the cycle-stability and the solubility in the electrolyte solvent was discussed.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

Selection and peer-review under responsibility of COE of Sustainable Energy System, Rajamangala University of Technology Thanyaburi (RMUTT)

Keywords: Organic cathode material; Lithium ion battery; Two-electron redox; Cycle-stability

1. Introduction

Rechargeable lithium batteries are currently indispensable power sources for daily-use portable electric devices. In the current battery system, rare-metal (minor metal) based positive-electrodes are typically used; therefore, the development of rare metal-free positive electrode materials and low-polluting safe materials is recently becoming more desirable due to the concern about their resource scarcity and

* Corresponding author. Tel.: +81-72-751-9651; fax: +81-72-751-9623.

E-mail address: m.yao@aist.go.jp.

environmental burden. One of the candidate categories is a series of redox active organic materials that contain no scarce metal resources [1–3].

Among the several types of organic positive-electrode materials, we have focused our attention on the benzoquinone-based materials, since the benzoquinone skeleton undergoes a two-electron redox reaction which can lead to a high discharge capacity up to about 500 mAh/g [4–6]. To develop the benzoquinone-based electrodes, anchoring the benzoquinone molecule in the electrode of batteries is imperative for its stable operation. We have found that low-molecular-weight crystalline benzoquinone derivatives tend to exhibit high utilization ratios during the initial charge/discharge cycles [7–12], in contrast to the polymer-type benzoquinone derivatives which show much lower capacities than the theoretical values [4–6]. However, the discharge capacities of the low-molecular-weight benzoquinone-based active materials tend to decrease upon cycling [9,11,13,14].

Previously, we have reported the battery performances of some benzoquinone derivatives bearing smaller alkoxy groups; *i.e.*, 2,5-dimethoxy-1,4-benzoquinone (DMBQ), 2,5-diethoxy-1,4-benzoquinone (DEBQ), and 2,5-di-*n*-propoxy-1,4-benzoquinone (DPBQ) (Fig. 1) [7,8]. While DMBQ maintained a relatively long cycling [7], DEBQ and DPBQ showed a poor cycle-stability [8]. Their cycle-stabilities are thought to result from the loss of the active materials from the electrode during cycling which is governed by the solubility of the benzoquinone molecules in the electrolyte solutions. One of the controllable and influencing factors of the solubility is the length of the alkoxy groups in these derivatives. In this study, we synthesized a benzoquinone bearing longer alkoxy chains, 2,5-di-*n*-decyloxy-1,4-benzoquinone (DDBQ), to make a comparison with the previous smaller alkoxy type benzoquinones. The effect of the long alkoxy chains on the cycle stability and the relationship between the solubility and the cycle-stability were discussed.

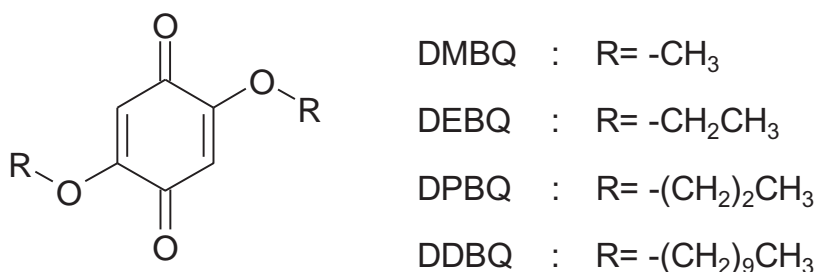


Fig. 1. Chemical structures of 2,5-dimethoxy-1,4-benzoquinone (DMBQ), 2,5-diethoxy-1,4-benzoquinone (DEBQ), 2,5-di-*n*-propoxy-1,4-benzoquinone (DPBQ), and 2,5-di-*n*-decyloxy-1,4-benzoquinone (DDBQ).

2. Experimental

2.1. Materials

2,5-Di-*n*-decyloxy-1,4-benzoquinone (DDBQ) was synthesized by the dehydration reaction of 2,5-dihydroxy-1,4-benzoquinone and 1-decanol (Tokyo Kasei Corp.) as described in the literature [15] and was purified by column chromatography. The density calculated from the crystallographic data is 1.1 g/cm³ [15].

2.2. Preparation of electrodes and cells

A positive-electrode composite sheet was first prepared by mixing the DDBQ powder, acetylene black as the conductive additive, and polytetrafluoroethylene as the binder in the weight ratio of 4:5:1 in a mortar. The sheet was then pressed onto a mesh-type aluminum current collector. The amount of active material was approximately 3 mg per electrode. The prepared positive-electrode and a lithium metal negative-electrode were placed in an IEC R2032 coin-type cell case with a glass filter as the separator. After the electrolyte solution of lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) / γ -butyrolactone (GBL) (1 M, 0.2 mL) was added, the cell case was sealed.

2.3. Measurements

Cyclic voltammetry (CV) was applied to the prepared electrode using an electrochemical analyzer (VersaSTAT-4, Princeton Applied Research). For this measurement, the coin-type cell described above was used. The voltammogram was recorded at the scan speed of 0.1 mV/s in the potential range of 1.5–3.5 V vs. Li⁺/Li at room temperature.

As for the battery test, the prepared coin-type cell was galvanostatically discharged at the current density of 20 mA per gram of benzoquinone with a cutoff voltage of 2.0 V vs. Li⁺/Li, and galvanostatically charged at the same current density with a cutoff voltage of 3.4 V vs. Li⁺/Li which was followed by a potentiostatic charge. The charge/discharge test was performed by a computer-controlled system (ABE system, Electrofield Co., Ltd.) equipped with a thermostatic chamber at 30°C. In this paper, the obtained capacities are expressed in terms of mass of the active material in the positive electrode.

2.4. Theoretical calculations

DFT calculations were performed using the GAUSSIAN 03 program package [16] to obtain theoretical insight into the electrochemical properties of the DDBQ-electrode. A hybrid functional of B3LYP [17,18] that includes a split valence basis set of 6-31G(d) was used for the geometry optimization of the monomer state of DDBQ. The calculated molecular orbitals were visualized by Gauss View 3.0 [19]. To estimate the electronic structure of the crystalline state, a single point calculation considering the periodic boundary condition (PBC) was performed using the coordinates extracted from the X-ray analysis [15] at the same B3LYP/6-31G(d) level.

3. Results and Discussion

3.1. Cyclic voltammetry

To evaluate the preliminary electrochemical properties of DDBQ, a CV measurement was first carried out for the prepared electrode (Fig. 2). Split peaks were observed at about 2.5 and 2.7 V vs. Li⁺/Li during the cathodic and anodic scans, respectively. The capacities calculated from the peak areas are 103 for the cathodic scan, and 117 mAh/g for the anodic scan. No stepwise redox behavior was clearly seen in the voltammogram; however, the obtained capacities are very close to the theoretical value of 128 mAh/g, which assumes the two-electron transfer reaction of DDBQ.

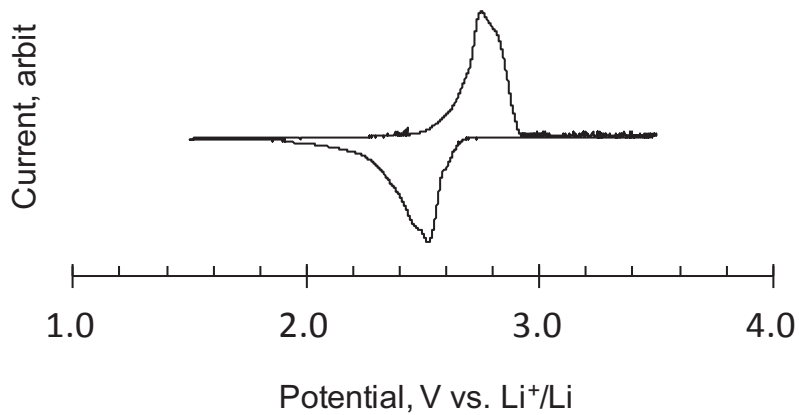


Fig. 2. Cyclic voltammogram of the DDBQ-electrode (Scan rate: 0.1 mV/s, Temperature: RT).

3.2. Initial Charge/discharge Behavior

Fig. 3 shows the first discharge and charge curves of the prepared DDBQ-electrode. The discharge curve consists of two plateau voltage regions at around 2.6 V and 2.5 V vs. Li^+/Li , corresponding to the cathodic process in the CV measurement. This behavior is considered to reflect the stepwise redox reaction between the neutral DDBQ and the dianion species. The observed potential difference between the two plateau regions during discharging is smaller than those of the previously reported smaller alkoxy group derivatives. The observed discharge capacity of 125 mAh/g well coincides with what estimated from the CV and is close to the theoretical value.

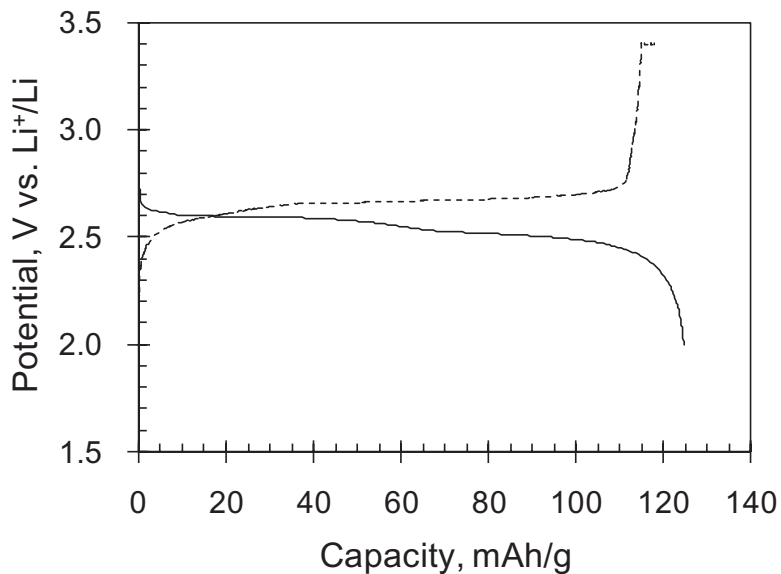


Fig. 3. Charge/discharge curves of the DDBQ-electrode (Current density: 20 mA/g, Temperature: 30°C).

3.3. Crystal Structure

Fig. 4 shows the crystal structure of DDBQ [15]. In the crystal, the molecules of DDBQ are stacked one-dimensionally by π - π interaction to form a column structure, which is also prominent in the DMBQ crystal. In the column, the mean intermolecular distance is 3.47 Å which is slightly larger than that of the DMBQ column (3.38 Å). In either case, the calculated values are close to the interlayer distance of graphite (3.35 Å). The calculated vertical area of each decyloxy-chain is about 0.2 nm², which is also comparable to the reported values of closely packed alkyl chains (0.15–0.25 nm²) [20].

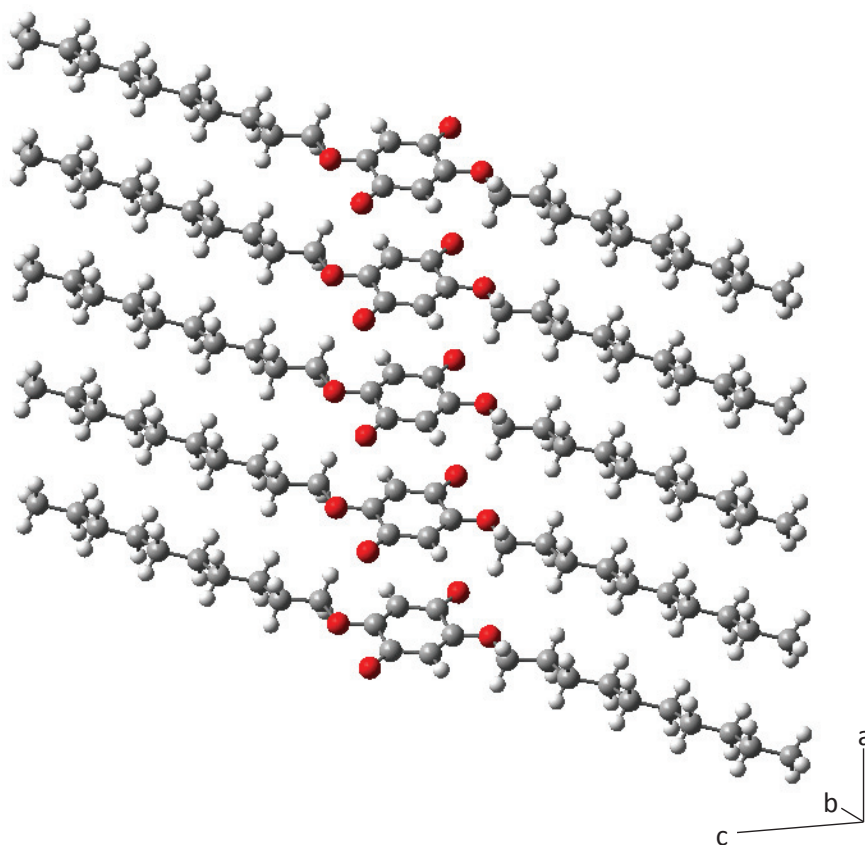


Fig. 4. Crystal structure of DDBQ (Crystallographic parameters, Crystal system: triclinic, Space group: *P*-1, $a=4.2118(3)$ Å, $b=5.3337(5)$ Å, $c=28.8117(19)$ Å, $\alpha=91.826(6)^\circ$, $\beta=92.775(5)^\circ$, $\gamma=92.992(7)^\circ$) [15].

3.4. DFT calculations

Furthermore, a DFT calculation was performed to obtain a theoretical insight into the electronic conduction mechanism of the crystalline state of DDBQ during the charge/discharge process. First, the calculated highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital

(LUMO) of the monomer state of DDBQ are shown in Fig. 5. Each molecular orbital has π -bond characteristics and is delocalized over the whole π -system of the benzoquinone moiety as in the case of the other alkoxy benzoquinones [7,8].

As an electronic state of the crystalline state, the density of state (DOS) was calculated along the π -stacked column of DDBQ. Fig. 6 shows the obtained DOS diagram. The energy levels of some orbitals expand, forming electronic band structures along the π -stacked direction due to the overlapping of the orbitals. The band at around -2.5 eV originated from the LUMO of the isolated monomer. Electrons can flow into the interior of the crystals along the formed electronic band during the discharging (reduction) process [7–11]. While the mechanism of the electronic and ionic conductions in the crystals has not yet been experimentally revealed, the formation of this electronic band structure can partially explain the high utilization of the electrodes for the series of the alkoxy benzoquinone derivatives during the charge/discharge processes.

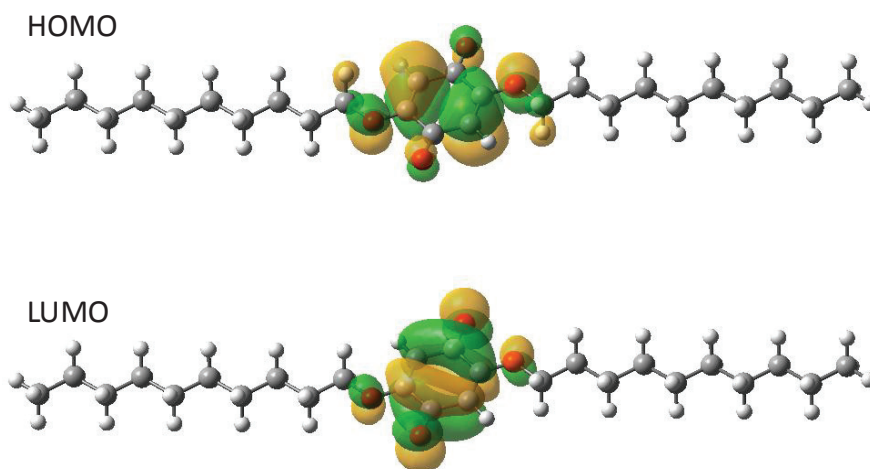


Fig. 5. Optimized structure of the monomer state of DDBQ and the calculated HOMO and LUMO. The geometries of these molecules are optimized at the B3LYP/6-31G(d) level.

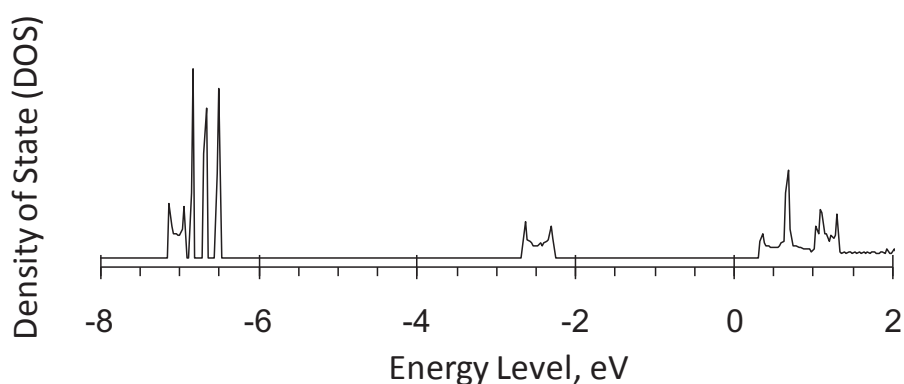


Fig. 6. Calculated density of state (DOS) along the stacked direction in the crystal of DDBQ. Computation was performed at the B3LYP/6-31G(d) level under the periodic boundary condition for the crystal coordinates.

3.5. Cycle-life performance

Finally, the result of a cycle-life test for the DDBQ electrode is shown in Fig. 7 along with those of the related compounds. The electrode of the dimethoxy derivative (DMBQ) did not show a drastic capacity decrease during the first 20 cycles; however, the cycle stabilities of the ethoxy derivative (DEBQ) and propoxy derivative (DPBQ) were poor. The decyloxy derivative (DDBQ) maintained 80 mAh/g after 20 cycles, which corresponds to 63 % of the initial capacity. The capacity retention of DDBQ is significantly higher than DEBQ and DPBQ, although slightly less than DMBQ.

As described in several reports on the battery performance of such low-molecular-weight compounds, their discharge capacities tend to significantly decrease upon cycling. One of the reasons for this capacity decay is the dissolution of the redox active molecules into the electrolyte. As for the solubility of the di-alkoxybenzoquinones, DDBQ is more soluble in GBL, the solvent used in the present study, than DMBQ, but less soluble than DEBQ and DPBQ; *i.e.*, the solubilities in GBL determined in the present study are 0.6, 1.0×10^2 , 2.5×10 , and 1.0 mg/cm^3 for DMBQ, DEBQ, DPBQ, and DDBQ, respectively. Although the origin of the lower solubility of DMBQ is not clear, the higher hydrophobicity of the long decyloxy group than the short alkoxy groups probably results in the lower solubility of DDBQ in the polar GBL solvent than those of DEBQ and DPBQ. Obviously, the cycle life of the electrode negatively correlates with the solubility of the benzoquinones, which strongly suggests that the electrode degrades through the loss of benzoquinone molecules leaching out of the electrode into the electrolyte. The structural flexibility of the DDBQ crystal brought by the long decyloxy chain may also play a role in the better durability of the electrode by alleviating the volume change in the crystal during the Li^+ insertion (discharge) and deinsertion (charge) processes.

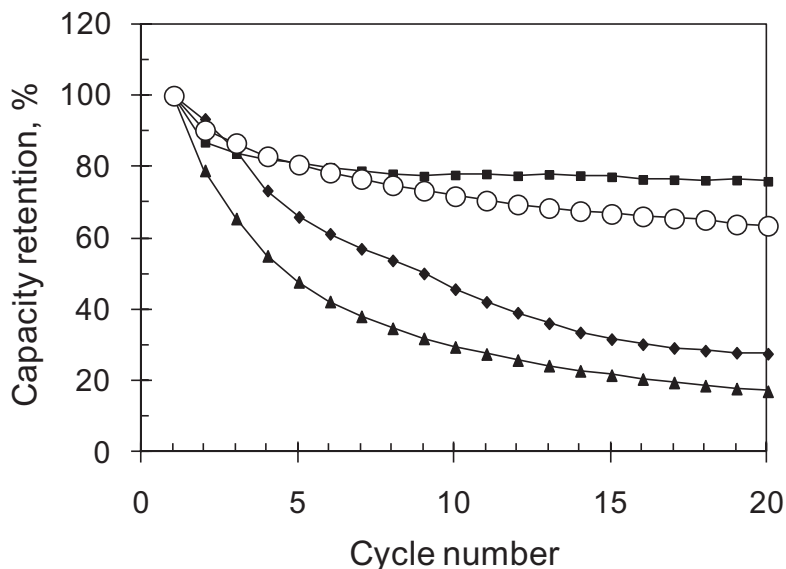


Fig. 7. Cycle-life performance of the electrodes using DDBQ and the related compounds (■: DMBQ, ▲: DEBQ, ◆: DPBQ, ○: DDBQ) (Current density: 20 mA/g, Potential range: 2.0–3.4 V vs. Li^+/Li , Temperature: 30°C).

4. Conclusion

The applicability of the redox reaction of a dialkoxybenzoquinone bearing long alkyl chains, 2,5-di-*n*-decyloxy-1,4-benzoquinone (DDBQ), was examined as a positive-electrode material for rechargeable lithium batteries. This material showed an initial discharge capacity of 125 mAh/g in the positive-electrode potential region of the rechargeable lithium batteries. The observed capacity corresponds to a two-electron redox behavior of the molecule. In the cycle-life test, the DDBQ-electrode performed better than the ethoxy and propoxy analogs and was similar to the methoxy analog.

A negative correlation between the cycle-stabilities and the solubility of the redox active molecules in the electrolyte solvent was observed by comparing DDBQ with other dialkoxybenzoquinones; *i.e.*, higher the solubility in the solvent, lower the cycle stability as a positive-electrode active material.

In order to develop a new organic active material that can tolerate many cycles, reducing the solubility in the electrolyte solution will be a key factor.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number 24750191.

References

- [1] Armand M, Tarascon JM. Building better batteries. *Nature* 2008; **451**: 652–657.
- [2] Nishide H, Oyaizu K. Toward flexible batteries. *Science* 2008; **319**: 737–738.
- [3] Novák P, Müller K, Santhanam SV, Hass O. Electrochemically active polymers for rechargeable batteries. *Chem Rev* 1997; **97**: 207–281.
- [4] Foos JS, Erker SM, Rembetsy LM. Synthesis and characterization of semiconductive poly-1,4-dimethoxybenzene and its derived polyquinone. *J Electrochem Soc* 1986; **133**: 836–841.
- [5] Gall TL, Reiman KH, Grossel MC, Owen JR. Poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene): a new organic polymer as positive electrode material for rechargeable lithium batteries. *J Power Sources* 2009; **119–121**: 316–320.
- [6] Song Z, Zhan H, Zhou Y. Anthraquinone based polymer as high performance cathode material for rechargeable lithium batteries. *Chem Commun* 2003; **4**: 448–450.
- [7] Yao M, Senoh H, Yamazaki S, Siroma Z, Sakai T, Yasuda K. High-capacity organic positive-electrode material based on a benzoquinone derivative for use in rechargeable lithium batteries. *J Power Sources* 2010; **195**: 8336–8340.
- [8] Yao M, Senoh H, Araki M, Sakai T, Yasuda K. Organic positive-electrode materials based on dialkoxybenzoquinone derivatives for use in rechargeable lithium batteries. *ECs Trans* 2010; **28(8)**: 3–10.
- [9] Yao M, Senoh H, Kuratani K, Sakai T, Kiyobayashi T. Organic rechargeable lithium batteries using anthraquinone-based positive-electrode: the effect of a molecular additive on the cycle-life performance. *ITE-IBA Lett* 2011; **4**: 52–56.
- [10] Yao M, Senoh H, Sakai T, Kiyobayashi T. 5,7,12,14-Pentacenetetrona as a high-capacity organic positive-electrode material for use in rechargeable lithium batteries. *Int J Electrochem Sci* 2011; **6**: 2905–2911.
- [11] Yao M, Yamazaki S, Senoh H, Sakai T, Kiyobayashi T. Crystalline polycyclic quinone derivatives as organic positive-electrode materials for use in rechargeable lithium batteries. *Mater Sci Eng B* 2012; **177**: 483–487.
- [12] Yao M, Araki M, Senoh H, Yamazaki S, Sakai T, Yasuda K. Indigo dye as a positive-electrode material for rechargeable lithium batteries. *Chem Lett* 2010; **39**: 950–952.
- [13] Senoh H, Yao M, Sakaebe H, Yasuda, K, Siroma Z. A two-compartment cell for using soluble benzoquinone derivatives as active materials in lithium secondary batteries. *Electrochim Acta* 2011; **56**: 10145–10150.
- [14] Hanyu Y, Honma, I. Rechargeable quasi-solid state lithium battery with organic crystalline cathode. *Sci Rep* 2012; **2**: 453.
- [15] Keegstra EMD, van der Mieden V, Zwikker JW, Jenneskens LW, Schouten A, Kooijman H, Veldman N, Spek AL. Self-organization of 2,5-di-*n*-alkoxy-1,4-benzoquinones in the solid state: molecular recognition involving intermolecular dipole-dipole, weak C=O=C hydrogen bond and van der waals interactions. *Chem Mater* 1996; **8**: 1092–1105.
- [16] Frisch MJ. et al. Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford, CT 2004.
- [17] Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* 1988; **38**: 3098–3100.
- [18] Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 1988; **37**: 785–789.
- [19] Dennington R II, Todd K, Millam J, Eppinnett K, Hovell WL, Ray G. GaussView, Version 4.1.2, Semichem, Inc., Shawnee Mission, KS, 2003.
- [20] Pomerantz M, Segmüller A. Coverage of Si substrates by self-assembling monolayers and multilayers as measured by IR, wettability and X-ray diffraction, *Thin Solid Films* 1985; **132**: 153–162.