doi:10.1246/cl.2011.750

High-performance Lithium Secondary Batteries Using Cathode Active Materials of Triquinoxalinylenes Exhibiting Six Electron Migration

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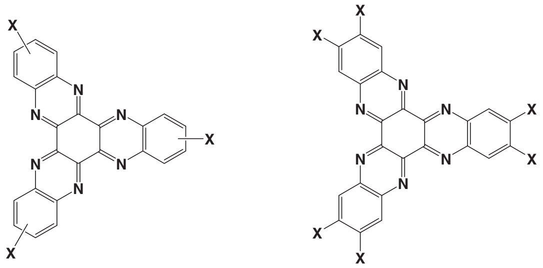
A coin cell battery is fabricated using triquinoxalinylene as a cathode active material and a lithium metal anode. The first discharge curve shows a remarkably large capacity (420 $\mathrm{A\,h\,kg^{-1}}$), which corresponds to a six electron migration in the first charge. However, repeating the charge–discharge until the 15th cycle gradually decreases the capacity, but after that the capacity remains constant with a value of 220 $\mathrm{A\,h\,kg^{-1}}$. This large value remains even after 100 cycles. Additionally, the use of a tribromo-substituted derivative gives a large discharge capacity ($\approx$250 $\mathrm{A\,h\,kg^{-1}}$) due to a comparatively stable six electron migration from the first charge–discharge cycle.

Lithium secondary batteries have emerged as high-performance rechargeable batteries with large capacities and high output voltages,[1] and are currently a common commercial battery.[2–6] However, lithium cobalt oxide ($LiCoO_2$), which was used as the first cathode active material in these batteries,[7] cannot complete a one electron migration during redox due to the drastic change in the crystal structures between $LiCoO_2$ and its oxidized species CoO_2, preventing the theoretical capacity (274 $\mathrm{A\,h\,kg^{-1}}$) from being realized. To increase the capacity above 400 $\mathrm{A\,h\,kg^{-1}}$, which the development of higher performing lithium secondary batteries now requires, active materials other than $LiCoO_2$ and related metal oxides continue to actively be sought. Organic compounds such as conducting polymers,[8,9] disulfide compounds,[10,11] stable neutral radicals,[12,13] electron-donating[14,15] and -accepting molecules[16,17] and metal clusters[18] have been expected to be active materials, since they can exhibit multiple electron migrations in their redox, providing the high capacities desired. Actually, secondary batteries based on these organic compounds as active cathode materials and on lithium metal as an anode have been fabricated, and their battery properties were investigated. Unfortunately, except for very few exceptions, these other batteries showed drawbacks of low capacities, low output voltages, and low stability of charge–discharge cycles.



1: X = H, F, Cl, Br

2: X = F, Cl

Chart 1. Molecular structures of **1**(X = H, F, Cl, Br) and **2**(X = F, Cl).

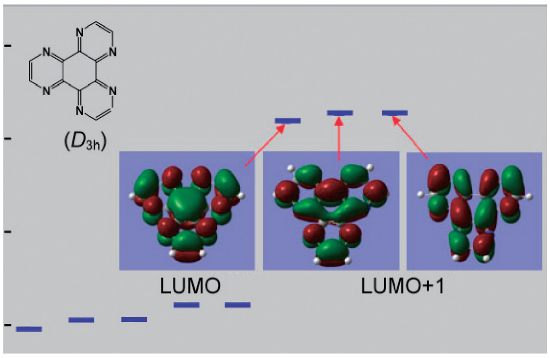


Figure 1. Energy levels of MOs of tripyradinylene and the atomic orbitals of LUMO and doubly degenerate (LUMO+1)s.

We noted that a promising cathode active material is triquinoxalinylene [**1**(X = H)] (Chart 1). The X-ray structure analysis of **1**(X = H) showed that the molecule has high planarity with D_{3h} symmetry. The MO calculation of the parent tripyradinylene (D_{3h}) (Figure 1) indicates that **1**(X = H) also possesses a very close to the lowest unoccupied (LU) molecular orbital (MO) and doubly degenerated next LUMOs (LUMO+1)s, suggesting a possible redox with a six electron migration. Herein coin cell batteries based on **1**(X = H) and its tri- [**1**(X = F, Cl, Br)] and hexahalogen-substituted derivatives [**2**(X = F, Cl)] (Chart 1) were fabricated. Among their charge–discharge tests **1**(X = H)- and **1**(X = Br)-based coin cell batteries exhibited remarkably large capacities of 250–420 $\mathrm{A\,h\,kg^{-1}}$, which correspond to six electron migrations in their redox. The syntheses of **1**(X = H, F, Cl, Br) and **2**(X = F, Cl) were carried out according to the literature.[19,20] The coin cell batteries were fabricated as follows. A mixture of **1**(X = H, F, Cl, Br) or **2**(X = F, Cl) vapor phase growth carbon fiber (conducting supporter), and poly(tetrafluoroethylene) (binder) (10:80:10 wt %) was well ground and pressed into a disk with a 12 mm diameter. Aluminum foil films (electric collectors), a polyethylene/polypropylene sandwich film (separator), and lithium metal (anode) were stacked consecutively above the cathode disk. A 1.0 M $LiPF_6$ solution in ethylene carbonate–diethyl carbonate (3:7, v/v) (electrolyte) was poured into the four-layer file and packaged. Figure 2A shows a cyclic voltammogram (CV) of a **1**(X = H)-based coin cell battery measured at 25 °C. Two pairs of peaks appeared at 2.36 and 2.69 V vs. Li/Li^+, which correspond to a two-step redox. The first and second steps probably involve two and four electrons, respectively. As is evident from the CV, the redox of **1**(X = H) was not stable and the peak intensity changed complicatedly by

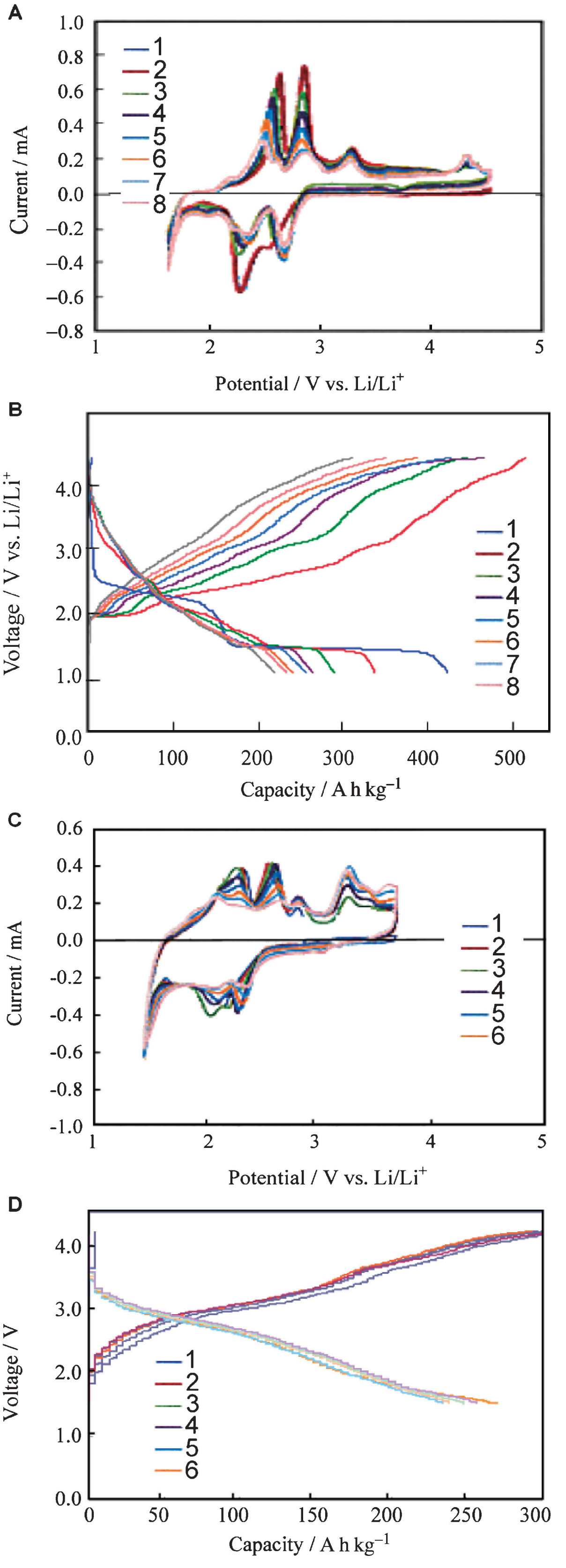


Figure 2. (A and C) Electrode CVs, and (B and D) charge–discharge cycles for **1**(X = H) and **1**(X = Br), respectively.

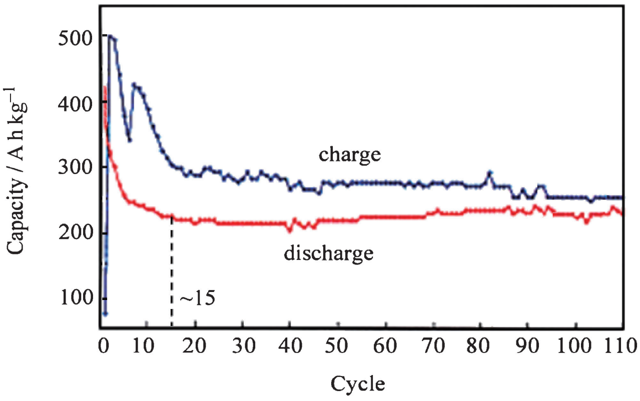


Figure 3. Cycle life of charge–discharge for **1**(X = H).

repeating the CV cycle. The charge–discharge test for the **1**(X = H)-based coin cell battery was performed in a voltage range of 1.5–4.2 V using a constant current of 0.1 mA. Figure 2B shows the first eight charge–discharge cycles. Consistent with the above electrode CV results, the first discharge was composed of two steps at output voltages of $\approx$2.3 and 1.6 V, respectively. The capacity of the first step was $\approx$140 A h kg^{-1}, which is close to the theoretical value (139 A h kg^{-1}) for a two electron redox migration. The second step had a capacity of $\approx$280 A h kg^{-1}, which is close to the theoretical value (279 A h kg^{-1}) due to a four electron migration. The overall capacity, which amounted to 420 A h kg^{-1}, is remarkably large and about twice as high as the maximum value (220 A h kg^{-1}) obtained by a high-performance lithium ion battery.[4]

After the second cycle, the first step was completely destroyed, while the second step was maintained until the fifth cycle, and then it was destroyed as well, which eventually gave rise to a gentle curve without steps. These changes in the discharge curves were accompanied by an overall decrease in capacity as the number of cycles increased. These changes in the discharge curves as the cycle number increases are due to the side reaction or irreversible redox of **1**(X = H) inside the coin cell battery and the gradual dissolution of **1** into the electrolyte solution. It should be noted that the discharge curves were gradually subjected to a small change after the sixth cycle.

The dependence of the charge–discharge number on the capacity, that is, the life cycle of the charge–discharge, was investigated until 110 cycles. Figure 3 shows the results. The capacity (420 A h kg^{-1}) obtained by the first discharge gradually decreased as the number of cycles increased during the first 15 cycles, but then became constant at 220 A h kg^{-1}. The value of 220 A h kg^{-1} is comparable to that obtained by a high-performance lithium ion battery and is still observed after 110 cycles. This result is of much interest with respect to a poly(4-hydroxy-2,2,6,6-tetramethylpiperidinyloxymethacrylate)-based organic radical battery, which exhibits a high stability in charge–discharge cycles, but has a low capacity (110 A h kg^{-1}). The electrode CVs and charge–discharge cycles also were investigated for **1**(X = F, Cl, Br)- and **2**(X = F, Cl)-based coin cell batterirs.[21] For the **1**(X = Br)-based coin cell battery, the electrode CV (Figure 2C) was comparatively stable and showed a two-step electron migration with nearly identical potentials as those of **1**(X = H)-based coin cell battery. The charge and discharge in the first cycle showed gentle curves without steps (Figure 2D), resembling the curves observed in the stable charge–discharge cycles for **1**-based coin cell battery. The overall capacity in the discharge was ≈250 A h kg^{-1}, which corresponds to the value (258 A h kg^{-1}) calculated for a six electron redox migration. Additionally, the output voltage was ≈1.6 V, which is the same as the value obtained by the **1**-based coin cell battery. This charge–discharge was comparatively stable after the multiple cycles. The other coin cell batteries also exhibited two-step electron migrations in their electrode CVs, but their charge–discharge was not stable in contrast to that of the **1**(X = Br)-based coin cell battery. The discharge capacities obtained after the first charge are 165–230 A h kg^{-1}, which correspond to 50–85% of the values calculated as six electron migration in their redox. In addition, repeating the charge–discharge cycles brought about gradual decrease in the capacities. However, in all the cases there was no change in the shape of charge–discharge curve by repeating the cycle, suggesting that these active materials are stable in the redox within the cathode, while they have stronger tendency to dissolve into the electrolyte than **1**(X = Br) by the charge–discharge cycle.

The six electron migrations in triquinoxalinylenes **1**(X = H) and **1**(X = Br) have not been observed in cathode active materials in previous secondary batteries, and these migrations provide a remarkably large capacity. However, the charge–discharge cycle stability as well as the output voltage need to be clarified. Nevertheless, the present findings advance the progress toward a practical organic lithium secondary battery using conductive polymers, neutral radicals, and metal clusters as well as the realization of electron-donating and -accepting molecules like triquinoxalinylenes as a cathode active material.[22]

This work was supported by a Grant-in-Aid for industry supporting projects from the Ministry of Economy, Trade and Industry. We thank Prof. Hiroshi Matsubara (Osaka Prefecture University) for the MO calculations.

References and Notes

1 T. Nagaura, K. Tozawa, *Prog. Batteries Sol. Cells* **1990**, *9*, 209.

2 *Litium Ion Betteries: Fundamentals and Performance*, ed. by M. Wakihara, O. Yamamoto, Kodansha/VCH, Weinheim, **1998**.

3 J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.

4 *Advances in Lithium-Ion Batteries*, ed. by W. A. van Schalkwijk, B. Scrosati, Kluwer Academic/Plenum, New York, **2002**.

5 M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652.

6 J. B. Goodenough, Y. Kim, *Chem. Mater.* **2010**, *22*, 587.

7 K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, *Mater. Res. Bull.* **1980**, *15*, 783.

8 P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid, A. J. Heeger, *J. Electrochem. Soc.* **1981**, *128*, 1651.

9 P. Novák, K. Müller, K. S. V. Santhanam, O. Haas, *Chem. Rev.* **1997**, *97*, 207.

10 S. J. Visco, C. C. Mailhe, L. C. De Jonghe, M. B. Armand, *J. Electrochem. Soc.* **1989**, *136*, 661.

11 M. Liu, S. J. Visco, L. C. De Jonghe, *J. Electrochem. Soc.* **1991**, *138*, 1891.

12 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351.

13 K. Nakahara, K. Oyaizu, H. Nishide, *Chem. Lett.* **2011**, *40*, 222.

14 H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, *J. Am. Chem. Soc.* **2009**, *131*, 8984.

15 W. Walker, S. Grugeon, O. Mentre, S. Laruelle, J.-M. Tarascon, F. Wudl, *J. Am. Chem. Soc.* **2010**, *132*, 6517.

16 J. S. Foos, S. M. Erker, L. M. Rembetsy, *J. Electrochem. Soc.* **1986**, *133*, 836.

17 M. Yao, H. Senoh, S. Yamazaki, Z. Siroma, T. Sakai, K. Yasuda, *J. Power Sources* **2010**, *195*, 8336.

18 H. Yoshikawa, C. Kazama, K. Awaga, M. Satoh, J. Wada, *Chem. Commun.* **2007**, 3169.

19 R. Nietzki, A. W. Schmidt, *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1227.

20 S. Barlow, Q. Zhang, B. R. Kaafarani, C. Risko, F. Amy, C. K. Chan, B. Domercq, Z. A. Starikova, M. Y. Antipin, T. V. Timofeeva, B. Kippelen, J.-L. Brédas, A. Kahn, S. R. Marder, *Chem.—Eur. J.* **2007**, *13*, 3537.

21 Supporting Information on coin cell battery structure, and CVs and charge–discharge cycles of **1**(X = F, C) and **2**(X = F, Cl) is available electronically on the Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

22 T. Sugimoto, *Kagaku (Kagaku Dojin)* **2011**, *66*, 48.