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Indigo Dye as a Positive-electrode Material for Rechargeable Lithium Batteries

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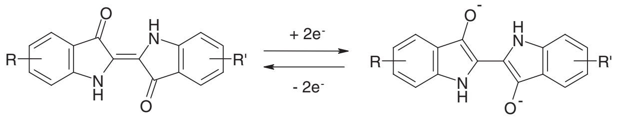
The performance of indigo carmine (5,5′-indigodisulfonic acid sodium salt) as a positive-electrode material for rechargeable lithium batteries was investigated. The prepared electrode showed an initial discharge capacity of 110 mA h g^{-1}, which corresponds to two-electron-redox behavior. Furthermore, the electrode was shown to have good cycle-life stability.

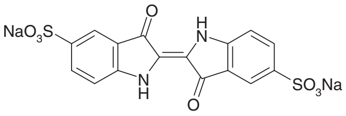
Indigo has been used for dyeing and printing, and its dark blue color has fascinated people all over the world since ancient times.[1–5] In particular, indigo is widely known as a dye for blue jeans. This dye is an organic compound with a heterocyclic structure and can be obtained from some plants. Several peripherally substituted derivatives are known and these indigo derivatives can be chemically reduced to form leuco-indigo derivatives (Scheme 1). In this reaction, the indigo skeleton undergoes two-electron reduction, and the resulting leuco-indigo can easily return to the original form by air oxidation. This reaction process is particularly important for dyeing since water-insoluble indigo becomes soluble via this reduction. Furthermore, this two-electron redox reaction has potential as an active material in batteries.[6] For rechargeable lithium batteries, which are widely used as power sources due to their high energy densities, inorganic compounds represented by lithium cobalt oxide ($LiCoO_2$) have been used as active materials in positive electrodes;[7] however, alternative low-polluting materials are becoming increasingly desirable owing to the consideration of environmental effects. Among several candidates, organic materials have recently been attracting attention since they do not contain expensive and harmful heavy metals.[7–18] Furthermore, these organic active materials are also noteworthy from the viewpoint of carbon neutrality, since some of them can be extracted from plants.[9,16]

As novel low-polluting organic active materials, we focused our attention on indigo derivatives and discovered that the water-soluble derivative indigo carmine (5,5′-indigodisulfonic acid sodium salt) (Scheme 2), which is used as a blue dye for food and drugs, shows an initial capacity density of above 100 mA h g^{-1} and relatively good cycle-life performance. In the present paper, the primary charge/discharge performance of indigo carmine as a positive-electrode active material will be described.

An R2032 coin-type sealed cell composed of a positive electrode incorporating indigo carmine and a negative electrode using a lithium metal sheet was prepared for battery tests. The weight ratio of indigo carmine powder, acetylene black as the conductive additive, and a poly(tetrafluoroethylene) binder was 4:5:1. The typical amount of the active material deposited on an aluminum mesh current collector was 3 mg. A mixed solution of ethylene carbonate and diethyl carbonate containing lithium hexafluorophosphate (1.0 mol L^{-1} $LiPF_6$ in EC/DEC = 1/1 by vol.) was used as an electrolyte solution. The charge/discharge tests were performed with computer-controlled systems equipped with a thermostatic chamber at 30 °C. In this paper, specific capacities were defined as the values per unit weight of active materials.



Scheme 1. Two-electron redox mechanism of indigo derivatives.



Scheme 2. Chemical structure of indigo carmine.

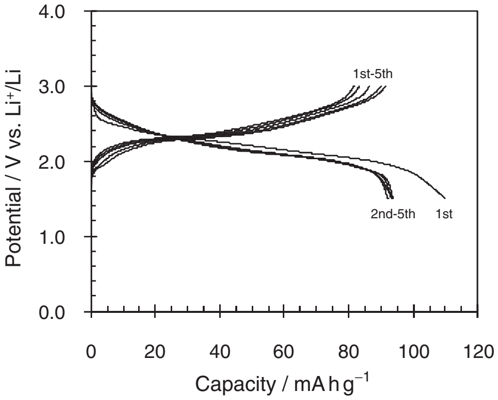


Figure 1. Charge/discharge curves of the electrode using indigo carmine at early cycles (Current density: 10 mA g^{-1}, Potential range: 1.5–3.0 V vs. Li^+/Li).

Figure 1 shows the first several charge/discharge curves of the electrode prepared using indigo carmine. Since indigo carmine itself has an oxidized structure, the electrode was initially discharged (Discharge reflects the reduction of indigo carmine in our case.). As shown, the electrode exhibits smooth discharge curves with an average potential of 2.2 V vs. Li^+/Li. There have been some studies on the redox potentials of indigo derivatives in organic systems, and the reported potentials can be converted to the range of 2.0–2.5 V vs. Li^+/Li.[3–5] This estimated potential range approximately agrees with the observed discharge potential in our measurement. The average potential of indigo carmine is lower than the average potential of conven-

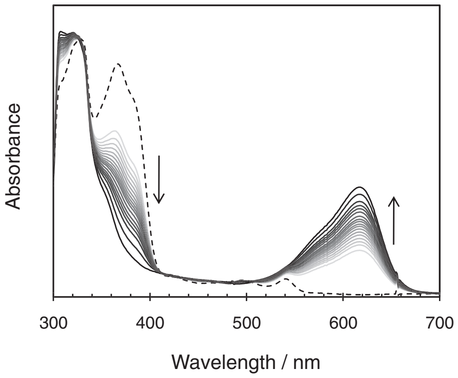


Figure 2. UV–vis spectral change of the extracted solution from the discharged electrode upon air oxidation. Degassed *N*,*N*-dimethylformamide containing small amount of organic acid was used as a solvent. Dashed line represents the spectrum of the reduced indigo carmine calculated from the obtained spectra.

tional positive-electrode materials such as lithium cobalt oxide ($LiCoO_2$) (3.8 V vs. Li^+/Li) or lithium iron phosphate (3.4 V vs. Li^+/Li); however, it is comparable to that of sulfide-based active materials (about 2 V vs. Li^+/Li). Stepwise plateau regions in the charge/discharge curves cannot be clearly seen in the charge/discharge curves, however, the obtained discharge capacity of $110\,mA\,h\,g^{-1}$ in the first cycle is extremely close to the theoretical value of $115\,mA\,h\,g^{-1}$ which assumes a two-electron redox reaction. Furthermore, ultraviolet–visible (UV–vis) spectroscopy was carried out for the extracted solution from the discharged electrode. Figure 2 shows the UV–vis spectral change of the solution upon air oxidation. A characteristic absorption band ascribed to the two-electron reduced "leuco form" was observed in the region of 350–400 nm.[4] The strength of this band decreased over time and a band around at 600 nm increases instead, which drives from the original "keto form" of indigo carmine. This observation also supports the two-electron redox reaction mechanism described in Scheme 1.

The obtained discharge capacity of indigo carmine is comparable to the practical capacity of an inorganic positive-electrode material of lithium manganese oxide ($LiMn_2O_4$) (100–$120\,mA\,h\,g^{-1}$), although it is somewhat smaller than the practical values of some conventional electrode materials such as $LiCoO_2$ ($140\,mA\,h\,g^{-1}$) and $LiFePO_4$ ($150\,mA\,h\,g^{-1}$). As a preliminary test, the battery performance of indigo itself was also examined under a similar condition. The electrode with indigo showed a discharge capacity of $200\,mA\,h\,g^{-1}$ with an average voltage of 2.3 V vs. Li^+/Li in the first cycle (Figure S1).[19] The obtained value is also quite close to the theoretical value of $204\,mA\,h\,g^{-1}$ which assumes a two-electron redox reaction (The variance of the theoretical capacities of indigo carmine and indigo itself reflects the difference in their molar masses: $M_{\text{indigo}} = 262.3$, $M_{\text{indigo carmine}} = 466.4\,g\,mol^{-1}$). However, the discharge capacity of indigo decreased rapidly upon cycling (Figure S2).[19]

The high-rate capability of the electrode using indigo carmine was examined by discharging at various current densities after several cycles. Figure 3 shows the relationship between the discharge capacity and the applied current density. The discharge capacity decreases as the current density increases, as is often seen for conventional electrodes. However, even at $1000\,mA\,g^{-1}$, which corresponds to a rate of about 10-C, the electrode showed 51% of the capacity observed at the low current density of $10\,mA\,g^{-1}$. The high-rate performances of electrodes using organic active materials have rarely been reported, with a few exceptions;[13] and the low electric conductively of typical organic compounds can be considered to negatively affect their high-rate performances. However, the obtained high-rate performance for indigo carmine is fair, and is comparable to that of an electrode incorporating commercially available $LiFePO_4$ in the same composition (In our measurement, an electrode prepared similarly using commercial $LiFePO_4$ gave a 55% capacity at the 10-C rate.). This high rate capability becomes worse to some extent by the reduction of conductive additive; however, it can be improved by the further optimization of the cell composition.

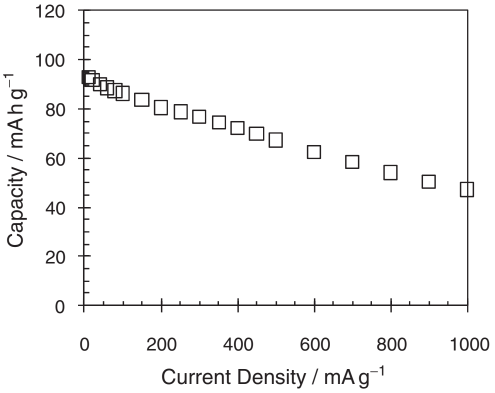


Figure 3. Rate capability of the electrode using indigo carmine (Cut-off potential: 1.5 V vs. Li^+/Li).

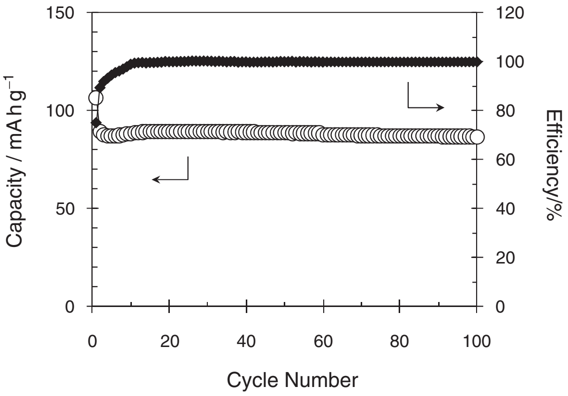


Figure 4. Cycle-life performance of the electrode using indigo carmine (Current density: $20\,mA\,g^{-1}$, Potential range: 1.5–3.0 V vs. Li^+/Li).

A conventional cycle-life test was also carried out for the prepared electrode. The capacity retention is shown in Figure 4. The capacity drops slightly after the initial cycle, and then the cell shows an almost constant value, and maintains $87\,mA\,h\,g^{-1}$ even after 100 cycles. In addition, the cell shows almost 100% Coulomb efficiency after about the 10th cycle. There have been a few reports on the battery performance of such low-molecular-weight compounds, and most of their discharge capacities decrease drastically upon cycling.[15–17] One of the reasons for this decrease in capacity is the dissolution of redox-active molecules into the electrolyte. In contrast, among low-molecular-weight organic active materials, the cycle-life performance of indigo carmine is relatively good. Indigo carmine shows a very low solubility for common organic solvents because of its high polarity due to the peripheral sulfonate sites, which should suppress the dissolution of the active material into the organic electrolyte during the charge/discharge process. An analysis of the electrolyte solution also revealed that the dissolution level of indigo carmine is very low even after a long-cycle (Figure S3)[19] (Indigo itself dissolves easily in the electrolyte after several cycles.). In addition, the high Coulomb efficiency implies the superior redox reversibility of this compound. These characteristic properties are considered to contribute to the fair cycle-life performance.

In this letter, we described the performance of indigo carmine (5,5′-indigodisulfonic acid sodium salt) as a positive-electrode active material using a coin-type sealed cell. Indigo carmine showed an initial discharge capacity of 110 $\mathrm{mA\,h\,g^{-1}}$, which corresponds to a two-electron redox reaction. Furthermore, the cycle-life performance was fair (87 $\mathrm{mA\,h\,g^{-1}}$ after 100 cycles) compared to those of other low-molecular-weight organic active materials.

The electrochemical properties of such organic materials can be adjusted by some chemical modifications, which would lead to further improvements of battery performance. In addition, the use of organic compounds derived from natural products as battery materials can reduce the environmental load. Compounds of this type may be utilized as alternative active materials for electronic power sources, and may some day replace conventional inorganic materials.

References and Notes

1 J. D. Roberts, M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, Inc., New York, **1965**, pp. 1052–1055.
2 A. J. Johnson, in *The Chemistry of Synthetic Dyes and Pigments*, ed. by H. A. Lubs, ACS Monograph Series No. 127, Reinhold, New York, **1955**, pp. 551–576.
3 P. A. Loach, in *Handbook of Biochemistry and Molecular Biology: Physical and Chemical Data*, 3rd ed., ed. by G. D. Fasman, CRC press, Cleveland, **1976**, Vol. 1, pp. 123–130.
4 A. M. Bond, F. Marken, E. Hill, R. G. Compton, H. Hügel, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1735.
5 G. Voss, M. Gradzielski, J. Heinze, H. Reinke, C. Unverzagt, *Helv. Chim. Acta* **2003**, *86*, 1982.
6 H.-K. Song, G. T. R. Palmore, *Adv. Mater.* **2006**, *18*, 1764.
7 J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.
8 H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737.
9 M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652.
10 M. Liu, S. J. Visco, L. C. De Jonghe, *J. Electrochem. Soc.* **1991**, *138*, 1891.
11 P. Novák, K. Müller, K. S. V. Santhanam, O. Hass, *Chem. Rev.* **1997**, *97*, 207.
12 K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro, E. Hasegawa, *Chem. Phys. Lett.* **2002**, *359*, 351.
13 K. Nakahara, J. Iriyama, S. Iwasa, M. Suguro, M. Satoh, E. J. Cairns, *J. Power Sources* **2007**, *165*, 398.
14 J. S. Foos, S. M. Erker, L. M. Rembetsy, *J. Electrochem. Soc.* **1986**, *133*, 836.
15 X. Han, C. Chang, L. Yuan, T. Sun, J. Sun, *Adv. Mater.* **2007**, *19*, 1616.
16 H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot, J.-M. Tarascon, *ChemSusChem* **2008**, *1*, 348.
17 Z. Song, H. Zhan, Y. Zhou, *Chem. Commun.* **2009**, 448.
18 W. Walker, S. Grugeon, O. Mentre, S. Laruelle, J.-M. Tarascon, F. Wudl, *J. Am. Chem. Soc.* **2010**, *132*, 6517.
19 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.