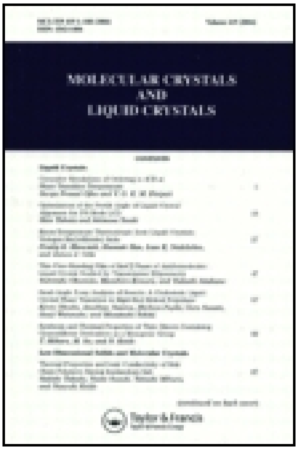

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Electrocrystallization as a Rechargeable Organic Battery

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Electrocrystallization as a Rechargeable Organic Battery

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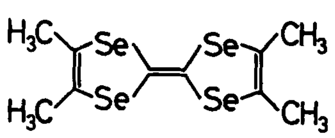
Electrocrystallization of conductive organic salts can be regarded as a charging process of a secondary battery. By use of a lithium metal as an anode, the following two organic batteries were made after electrocrystallization, *i.e.*, Li|LiClO$_4$ in THF|(perylene)-ClO$_4$, and Li|LiClO$_4$ in THF|(tetrathianaphthalene) · ClO$_4$. All-solid state organic battery, Li|poly(ethylene oxide) + LiClO$_4$|(tetrathianaphthalene) · ClO$_4$, was always made. Their charge and discharge characteristics were discussed.

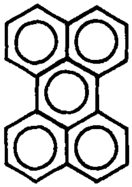
1. INTRODUCTION

The studies on the highly conductive organic materials have progressed greatly in the last few years.[1,2] The electrocrystallization technique has received much attention,[3] because the complexes of tetramethyltetraselenafulvalene (TMTSF) obtained by this method were discovered to be the first organic superconductors.[4] From another viewpoint of the electrocrystallization, electricity is stored as an insoluble conductive complex. Thus, the electrocrystallization is regarded as a charging process of batteries. Upon connecting two electrodes after electrocrystallization, a reverse electrochemical reaction gives rise to an external current. Thus, the electrocrystallization cell can be regarded as a secondary battery. The highly conductive property required for the electrode material is satisfied in this case.

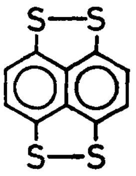
We have applied the complex of perylene or 1,4,5,8-tetrathianaphthalene (TTN), obtained by an electrochemical method, to a new type of organic battery. We have made the following two batteries



TMTSF



Perylene



TTN

after electrocrystallization, *i.e.*, Li|LiClO$_4$ in THF|(perylene)-ClO$_4$, and Li|LiClO$_4$ in THF|(TTN) · ClO$_4$. As an extention of these studies, we have also made an all-solid state battery, Li|poly(ethylene oxide) + LiClO$_4$|(TTN) · ClO$_4$. The characteristic points of these batteries are discussed below.

2. EXPERIMENTAL

2.1. Materials

Perylene was purified by vacuum sublimation. TTN was synthesized by the reported procedures.[5] It was purified by vacuum sublimation. Poly(ethylene oxide) (MW = 5×10^6) was supplied by Yahata Chemicals Co. Ltd. Tetrahydrofuran (THF) was purified by refluxing it over calcium hydride, followed by distillation.

2.2. Fabrication of Batteries

All manipulations were performed under argon atmosphere. Platinum plate electrode and platinum wire electrode were mounted inside a glass vessel through a rubber cock. Lithium metal was pressed to the platinum wire electrode and fastened to it by a gold wire. THF solution (40 ml) containing lithium perchlorate (0.5 mol dm^{-3}) and donor molecule (50 mg) was poured into the electrochemical cell. Charge and discharge of the cell were performed under a galvanostatic condition by use of a Potentiostat/Galvanostat HA-501 (Hokuto Denko Ltd).

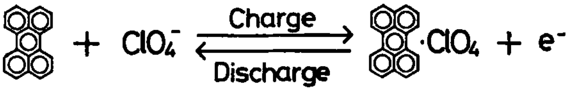
2.3. All-solid State Battery

Poly(ethylene oxide) (0.4 g) and LiClO$_4$ (0.215 g) were dissolved in acetonitrile (3 ml). After standing for one day, the viscous solution was cast onto a teflon plate, and was allowed to stand for 12 hrs. It was then dried by heating at 60 °C in the air for 12 hrs and finally in dynamic vacuum for one day at 60 °C. It was then stripped off as a film. The TTN complex was pressed to the pellet (4 mm diameter and 0.17 mm thickness). The solid electrolyte film was sandwiched between the pellet of TTN-complex and Li foil in an argon atmosphere. The whole was finally pressed tightly inside two teflon plates by using bolts and nuts. The discharge curve of the battery was measured under an argon atmosphere.

3. RESULTS AND DISCUSSION

3.1. Li-Perylene Salt Battery

Before electrocrystallization began, an open circuit voltage (V_{oc}) of 3.1 V had been observed between lithium and platinum electrodes. Figure 1 shows the charge and discharge characteristics of the Li-perylene salt battery. The platinum and lithium electrodes were connected with the positive and negative terminals of the power source. When electrocrystallization started under a galvanostatic condition (80 μA), an almost constant charging voltage (4.1 V) was observed. Black microcrystalline complexes were gradually deposited on the surface of the platinum plate as reported by H. J. Keller *et al.*[6] Stable V_{oc} of 4.0 V was observed after electrocrystallization for 12 hrs. This value is consistent with the difference of the redox potentials between perylene/perylene$^+$ and Li/Li$^+$.[7] The discharge curve of the battery under galvanostatic conditions (80 μA) showed relatively flat voltage (3.7 V), followed by an abrupt voltage drop (Figure 1). The electrochemical reactions of the battery are as follows.



$$Li^+ + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} Li$$

During discharge, some crystals of perylene salts were found to drop off from the platinum plate. This phenomenon is caused by the fact that the reduction of the perylene salt occurs mainly at the roots of the crystals, thus solubilizing the contact parts of the organic salts to the platinum electrode. In other words, all of the cathode active

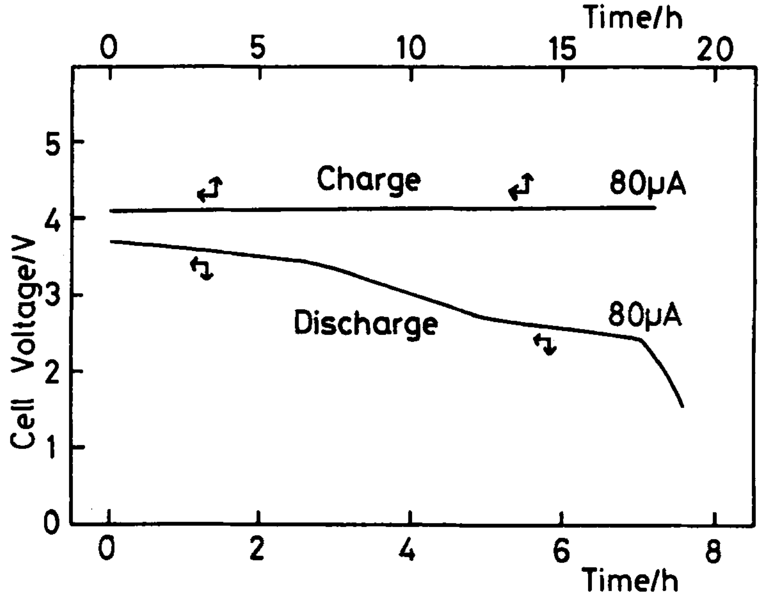


FIGURE 1 Charge and discharge curves of Li-perylene salt battery under galvanostatic conditions (80 μA).

materials could not be used during discharge. Thus, the Coulombic efficiency, so far, is only 40%. If the conductivity of organic salt were much larger, the reduction of the salt would occur at the surface of the complex, which might give higher Coulombic efficiency. The gradual decrease of a discharge voltage after 3 hrs is attributed to an increase of the overvoltage caused by the decrease of the contact area of the perylene salts to the platinum plate.

3.2. Li-TTN Battery

The present system also gave charge and discharge curves similar to Figure 1 under galvanostatic condition. Just after electrocrystallization for 12 hrs, V_{oc} of 3.5 V was observed. This value is also consistent with the difference of the redox potentials between TTN/TTN$^+$ and Li/Li$^+$.[7] However, the V_{oc} was unstable and decreased to 3.3 V during 1 hr. The Coulombic efficiency was very low (0.2%). The instability of V_{oc} and low Coulombic efficiency are due to the facts that the complexes deposited on the platinum plate dissolved gradually in THF,[8] and that the TTN complexes dropped off from the platinum plate during discharge for the same reason as that described in the Li-perylene salt battery.

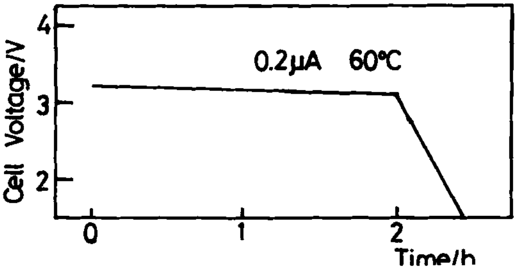


FIGURE 2 Discharge curve of an all-solid state battery under galvanostatic conditions (0.2 μA) at 60 °C.

3.3. All-solid State Battery

As an extention of the above studies, an all-solid state organic battery was fabricated by using a poly(ethylene oxide) film containing $LiClO_4$ as solid electrolyte.[9] TTN · ClO_4 obtained by electrocrystallization and Li metal were used as cathode and anode active materials, respectively. A stable V_{oc} (3.3 V) was observed at 60 °C.[10] Figure 2 shows the discharge curve of the battery at 60 °C under galvanostatic conditions (0.2 μA). A relatively flat voltage (3.2 V) could be obtained. The electrochemical reaction can be described as follows.

$$\mathrm{TTN} \cdot \mathrm{ClO_4} + \mathrm{Li^+} + e^- \rightarrow \mathrm{TTN} + \mathrm{LiClO_4}$$

$$\mathrm{Li} \rightarrow \mathrm{Li^+} + e^-$$

Thus, the organic complexes obtained by electrocrystallization could also be used as the electroactive materials of all-solid state battery.

4. SUMMARY

Electrocrystallization of conductive organic salts can be regarded as a charging process of a secondary battery. After electrocrystallization, reverse electrochemical reaction gave rise to an external current by connecting both electrodes. Two batteries were fabricated by using Li metal as an anode active material, and perylene complex or TTN complex as a cathode active material. The most serious problem of these batteries is that the electrochemical reaction of discharge occurs mainly at the roots of the crystals, giving rise to detachment of the complex from platinum. Thus, Coulombic efficiency was low. We could also fabricate an all-solid state organic battery. Although the above-mentioned disadvantage must be conquered for the practical application, the present systems are new and attractive organic batteries of technological importance.

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References

1. J. S. Miller ed., "Extended Linear Chain Compounds" (Plenum Press, New York 1982), vol 1, 2.
2. L. Alcacer ed., "The Physics and Chemistry of Low-dimensional Solids", (Dordrecht 1980).
3. E. M. Engler, R. Green, P. Haen, Y. Tomkiewicz, K. Mortensen, and J. Berendzen, *Mol. Cryst. Liq. Cryst.*, **79**, 15 (1982).
4. D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Physique Lett.*, L95 (1980).
5. F. Wudl, D. E. Schafer, and B. Miller, *J. Am. Chem. Soc.*, **98**, 252 (1976).
6. H. J. Keller, D. Nöthe, H. Pritzkow, D. Wehe, M. Werner, P. Koch, and D. Schweitzer, *Mol. Cryst. Liq. Cryst.*, **62**, 181 (1980).
7. The electrochemical half-wave potentials of perylene and TTN were measured *vs* SCE at a platinum electrode in THF-Bu_4NClO_4 (0.1 mol dm^{-3}): perylene, $E_{1/2}$ = 1.03 V, 1.25 V *vs* SCE; TTN, $E_{1/2}$ = 0.55 V, 0.93 V *vs* SCE. The potential of Li/Li^+ was −2.96 V *vs* SCE in THF.
8. T. Nogami, H. Tanaka, S. Ohnishi, Y. Tasaka and H. Mikawa, *Bull. Chem. Soc. Jpn.*, in press.
9. R. Dupon, B. L. Papke, M. A. Ratner, D. H. Whitmore, and D. F. Schriver, *J. Am. Chem. Soc.*, **104**, 6247 (1982).
10. We could not observe the cell voltage below 60 °C, because of the low ionic conductivity of the solid electrolyte.