**ABSTRACT:** Rare-metal-free and high-performance secondary batteries are necessary for improving the efficiency of renewable energy systems. Organic compounds are attractive candidates for the active material of such batteries. Many studies have reported organic active materials that show high energy density per active material weight. However, organic active materials, most of which exhibit low conductivity and low specific density, typically require a large amount of a conductive additive (>50 wt %) to obtain a high utilization rate. Therefore, organic active materials rarely display high energy density per electrode weight. High energy densities per electrode weight can be obtained using high weight fractions of active materials and low weight fractions of conductive additives. Herein, we report that a low-conductivity organic active material, indigo, showed improved net discharge capacity density when even a small amount of a conductive polymer composite, poly(3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT/PSS) with D-sorbitol, was used as both a binder and conductive additive. The cycle life was also improved by coating one side of the separator with the composite, which probably hindered the dissolution of the active material. A discharge capacity of 96% of the theoretical capacity of indigo and an improved cycle life were achieved with an electrode containing 80 wt % indigo and with a PEDOT/PSS-coated separator. The optimal fraction of the conductive binder was examined, and the mechanism of conductivity enhancement was discussed. The present scheme allows us to replace the dispersion solvent of the slurry, N-methylpyrrolidone, with water, which can reduce the environmental load during battery manufacturing processes.

**INTRODUCTION**

In recent years, the demand for improved battery performance has emerged based on renewable energy storage requirements. Lithium batteries have attracted increasing attention for these applications due to their high energy density. Attention has been devoted not only toward improving the performance of batteries but also to the safety, resource limitations, and environmental considerations. Sulfur and organic compounds have attracted attention as potential candidates for use as the active material in high-performance batteries. While sulfur has a very large capacity, organic compounds can be tuned according to their working voltage. Organic compounds with low molecular weight that undergo a multi-electron transfer redox reaction exhibit higher theoretical capacity and energy density than organic compounds with high molecular weight and conventional metal oxides. Many compounds have been reported with high initial capacity densities exceeding 200 mAh g\(^{-1}\). To obtain such high capacities, organic active materials with a low electric conductivity require large amounts of conductive additives and associated binders to fix them. Therefore, organic active materials rarely display high energy density per electrode weight. Despite reported high capacities, the capacity per electrode for organic active materials hardly exceeds that of their conventional metal oxide counterparts. High energy densities per electrode weight can be obtained using high weight fractions of active materials and low weight fractions of conductive additives. To effectively utilize the active material with low weight fractions of conductive additives, an increase in the conductivity of organic active materials is needed. The combustion carbon coating performed at high temperatures is effective for metal oxide electrodes but may damage the organic compounds. Thus, another less-damaging method is required to increase the conductivity of organic active materials.

Organic compounds with low gravimetric densities have lower volumetric fractions of carbon additives than inorganic materials with high gravimetric densities, which results in poorer contact between the active material and the carbon additive. The low gravimetric density of organic active materials partially explains the need for significant amounts of conductive additives.

A conductive polymer, poly(3,4-ethylenedioxythiophene)/polystyrene sulfonic acid (PEDOT/PSS) (Figure 1), was reportedly used as a conductive additive and a binder to enhance the electric conductivity of a Si electrode. It was also reported that PEDOT/PSS film suppresses the capacity.
deterioration of sulfur cathodes, which are attracting attention for use as high-capacity cathodes. PEDOT/PSS films have been shown to suppress the dissolution of some organic active materials in contact with the electrolyte and therefore to improve the battery cycle life. In addition, PEDOT/PSS was reported to have a low environmental impact as it contains no fluorine. As PEDOT/PSS is highly dispersible in water, it is possible to further reduce the environmental burden associated with electrode manufacturing by preparing electrode slurries using water as the dispersion solvent instead of N-methylpyrrolidone (NMP), which is a REACH (European Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals)-restricted organic solvent with a high environmental load.

To resolve the aforementioned issues and to develop an electrode, which uses an organic active material, with high capacity per weight of active material, we focused on PEDOT/PSS. PEDOT/PSS was used in our previous study as a conductive binder for a QTTFQ triad (Q: p-benzoquinone, TTF: tetrathiafulvalene) active material. A sugar alcohol, D-sorbitol, was added to PEDOT/PSS to enhance its conductivity. In the wake of our PEDOT/PSS study, we intend to investigate the extent to which the weight fraction of the organic active material can be increased by using indigo, which is a mundane natural dye with a two-electron redox process (Figure 1). Here, it should be noted that the polymer-coated separator was used instead of a conventional glass filter, the initial discharge capacity was 148 mAh g⁻¹, which was 73% of the theoretical capacity, and the average initial discharge voltage was 2.1 V (Figure 3b). The behavior of the first discharge curve was very similar to that of the curve without the polymer-coated separator. The polymer-coated separator improved the cycle life. The coulombic efficiency of the cell with the polymer-coated separator was equivalent to that of the cell with the conventional glass filter. Here, it should be noted that the polymer-coated electrode capacity was 1.5 times higher than the capacity of the electrode with the glass filter over 20 cycles (Figure 3c), implying that the dissolution of the active material was suppressed by the polymer-coated separator.

**RESULTS AND DISCUSSION**

**Cell Performance of the PTFE-Type Electrodes.** Figure 2a shows the charge–discharge curve of the Li half-cell with the [40 wt %-indigo/PTFE] electrode with a conventional glass filter, and Figure 2b shows the relationship between the initial discharge capacity densities per active material weight and its content in the electrode. The initial discharge capacities of the [40 wt %-indigo/PTFE] and the [60 wt %-indigo/PTFE] electrodes were 187 and 134 mAh g⁻¹, respectively, with an average voltage of 2.2 V for both. The initial discharge capacity of the [80 wt %-indigo/PTFE] electrode was less than 1 mAh g⁻¹. When PTFE was used as the binder, the active material content was restricted to a low amount (<60 wt %), resulting in a very low actual net capacity density per electrode weight. The discharge capacity of the [40 wt %-indigo/PTFE]/Li cell at the 20th cycle was 75 mAh g⁻¹, and the coulombic efficiency for the [40 wt %-indigo/PTFE]/Li cell was nearly 95% after the third cycle (Figure 2c).

![Figure 1. (a) Structures of PEDOT/PSS, D-sorbitol, and indigo. (b) Redox process of indigo.](https://dx.doi.org/10.1021/acsomega.0c00313)
Cell Performance of the PEDOT-Type Electrodes. The charge–discharge characteristics of the [80 wt %-indigo/PEDOT]/Li cell with a glass filter were evaluated (Figure 4a). The initial discharge capacity of the [80 wt %-indigo/PEDOT]/Li cell with the glass filter was 197 mAh g\(^{-1}\), with an average voltage of 2.0 V. Using the PEDOT-type electrode, the initial discharge capacity of the cell was maintained at 96% of its theoretical capacity (204 mAh g\(^{-1}\)), indicating two electrons were considered to be used per molecule. After initial discharge, the charge capacities and discharge capacities are less than half of the initial capacity. Since indigo does not dissolve much in the electrolyte solution in its neutral state, dissolution is expected in the two-electron reduced state. The coulombic efficiency exceeds 100% because of residual capacity during the discharging process at earlier cycles.

Figure 4b shows the initial discharge capacity density per active material weight as a function of its content in the electrode using the conventional glass filter. A maximum initial discharge capacity occurred at an active material content of 80 wt %. A decrease in the capacity as the active material content increased from 80 to 90 wt % implied the presence of an upper limit in the fraction of active material in the electrode, the electronic conduction of which was sustained by PEDOT/PSS. Meanwhile, the reason for the electrode with 60 wt % content had a lower capacity than that of the 80 wt % content is presently not clear. It can, nonetheless, be speculated that, while PEDOT/PSS is certainly electron conductive, an excessive amount of PEDOT/PSS may clog the Li-ion conduction by covering the particles of the active material. A similar phenomenon was reported in the case of LiFePO\(_4\) which has a low electron conductivity.\(^4\) Although the carbon coating on LiFePO\(_4\) was effective in improving the electron conductivity, the movement of Li ions seemed to be hindered when the carbon film was too thick. Like carbon membranes, PEDOT/PSS binders may also alienate ionic conduction when present in large amounts in the electrode. In the present study, only 20 wt % PEDOT/PSS seemed to be optimal for balancing the electronic and ionic conductivities of the electrode.

Figure 4c shows the charge–discharge curves of the [80 wt %-indigo/PEDOT]/Li cell with polymer-coated separators. The initial discharge capacity was 197 mAh g\(^{-1}\), with an average voltage of 1.9 V. The initial discharge curve displays similar behavior to that with the conventional glass fiber separator from the viewpoint of voltage and capacity.

Figure 4d shows the initial discharge capacity density per active material weight as a function of its content in the electrode using the polymer-coated separator. A maximum initial discharge capacity occurred at an active material content of 80 wt %, whose tendency is the same as that with glass fiber filter, indicating the same mechanism as that with glass fiber filter is functioning.

The polymer-coated separator drastically improved the cycle life; the cycle efficiency was around 100% (Figure 4e). There are similar reports of the cyclability of organic active materials and sulfur improving using a PEDOT/PSS film.\(^2\)–\(^5\) Wang et al.\(^6\) and Kiya et al.\(^7\) reported that the PEDOT/PSS film prevented the organic active materials from dissolving in the electrolyte both physically and electrostatically. A similar mechanism may be at play in the present study. Another organic active material 1,1'-iminoanthraquinone (IDAQ) was also applied to the combination of the PEDOT/PSS conductive binder and coated separator (Table S1). The [80 wt %-IDAQ/PEDOT]/Li cell with a coated separator showed a good cycle life (Figure S2), indicating the wide applications of combining the PEDOT-type electrode and coated separator.

The cross-sectional FE-SEM images of the [80 wt %-indigo/PVdF] electrode and the [80 wt %-indigo/PEDOT] electrode...
before cell assembly are shown in Figure 5. For the PVdF-type and PEDOT-type electrodes, the loading of the active material was about 0.5 ± 0.1 mg cm⁻². The thickness of the [80 wt %-indigo/PEDOT] electrode was half of that of the [80 wt %-indigo/PVdF] electrode, despite their similar active material loading, suggesting that PEDOT/PSS was capable of increasing the volumetric energy density of the electrode.

Comparison of the Three Electrodes. Among the electrodes with 80 wt % active material content, the PEDOT-type electrode had the highest initial discharge capacity, followed by the PVdF- and PTFE-type electrodes. The PVdF-type electrode outperformed the PTFE-type electrode, probably because, albeit containing equal amounts of indigo, the former contained more conductive additive and less binder, i.e., an insulator, than the latter did (see Table 4).

The discharge capacity density per active material of the [80 wt %-indigo/PVdF] electrode was lower than that of the [40 wt %-indigo/PTFE] electrode and was as large as that of the [60 wt %-indigo/PTFE] electrode. This result is related to the dispersibility of the components and the resulting electron conductivity in the electrode bulk, which can be affected by the electrode manufacturing method (manual or mechanical) and the binder used. It is suggested that the PVdF-type electrode is a more appropriate choice than the PTFE-type electrode to increase the capacity per electrode weight using organic active materials.

Further, we compared the two coating electrodes of [80 wt %-indigo/PVdF] and [80 wt %-indigo/PEDOT]. The initial discharge capacities of the [80 wt %-indigo/PVdF] and [80 wt %-indigo/PEDOT] electrodes were 71 and 96% of the theoretical capacity of indigo, respectively. The origin of the difference will be discussed subsequently from the viewpoint of sufficient dispersion of material constituents in the two electrodes. It should be the volume, and not the weight, that matters for the conductive agent to provide the appropriate spatial dispersion for the active materials. The specific density of each material is summarized in Table 1. Then, the volume ratios of the materials in the [80 wt %-indigo/PVdF] and [80 wt %-indigo/PEDOT] electrodes were calculated and are summarized in Table 2. Examination of the volume ratio of the electrode constituents, shown in Table 2, revealed that the conductive component occupied 2.3 times more volume in the PEDOT-type electrode than in the PVdF-type electrode. Furthermore, the size of AB secondary particle was greater than that of the water-dispersed PEDOT/PSS colloid, the agglomeration of which was suppressed by D-sorbitol as a plasticizer.42 Further, the active material was more effectively surrounded by conductive agents in the PEDOT-type electrode than in the PVdF-type electrode.

In addition, the addition of D-sorbitol has been reported to enhance the adhesivity and elasticity of PEDOT/PSS.40–42 These effects would also favor the PEDOT-type electrode in extracting as high as 96% of the theoretical capacity of indigo. Figure 6 illustrates how the electrode components are distributed in the PVdF- and PEDOT-type electrodes.

Table 1. Density of the Electrode Components

| Component        | indigo | AB  | PTFE | PVdF | PEDOT/PSS | D-sorbitol |
|------------------|--------|-----|------|------|-----------|------------|
| Density (g cm⁻³) | 1.54   | 2.1 | 2.2  | 1.8  | 1.0       | 1.5        |

Table 2. Volume Fraction of Materials in the 80 wt %-Indigo/PEDOT and 80 wt %-Indigo/PVdF Electrodes Calculated from Tables 1 and 4

| Electrode          | indigo (vol %) | AB (vol %) | PTFE (vol %) | PVdF (vol %) | PEDOT/PSS (vol %) | D-sorbitol (vol %) |
|--------------------|----------------|------------|--------------|--------------|------------------|-------------------|
| 80 wt %-indigo/PEDOT | 72             | 25         | 4            | 3            |                  |                   |
| 80 wt %-indigo/PVdF  | 84             | 11         | 4            |              |                  |                   |

Prospects. This study investigated the potential of organic batteries utilizing the PEDOT-type electrode fabrication method. Usually, the electrodes of organic batteries require large quantities of conductive additives, which reduces the fraction of active material in the electrode to less than 50 wt %. In this study, we fabricated an electrode containing 80 wt % of active material, which showed a relatively high utilization ratio of the active material. In this section, the conventional and presented organic material electrodes are compared to a conventional inorganic electrode, i.e., using lithium iron phosphate and lithium cobalt oxide. When the fraction of organic active material in the electrode increased up to 80 wt %, the energy density of the electrode increased by 1.6 times. It appears that the energy density of the organic battery rivals that of contemporary inorganic material systems, as shown in Table 3. As far as gravimetric energy density is concerned, the organic battery exhibited better performance than that of the inorganic battery, under the assumption that organic materials with capacity as high as 400 mAh g⁻¹ and working voltage as high as 3 V vs Li_CE were established. Furthermore, as shown in the FE-SEM observation section, PEDOT-type electrodes have...
the possibility to increase the volumetric energy density per weight of electrode compared to that of PVdF-type electrodes. Thus, the performance of organic batteries can rival that of inorganic batteries in terms of volumetric energy density and gravimetric energy density.

This study demonstrated that coating the separator with a conductive polymer was effective for stopping the shuttling of the organic compound. There may be a limit, however, to preventing the organic materials from eluting into the electrolyte by only modifying the separator. Other approaches that can improve the cycle characteristics are oligomerization and polymerization of organic molecules and application of solid electrolyte. In this study, indigo was used as a representative organic active material. The redox potential of indigo could be lower for a general cathode and used as a representative organic active material. The redox potential of indigo could be lower for a general anode. However, the redox potential of the organic electrodes can be tuned by introducing an electron-withdrawing substituent to increase the potential and an electron-donating substituent to lower the potential. In the case of oligomers linked to the same redox-active unit, controlling the distance between the units is effective for tuning the average potential.

Like D-sorbitol, other sugar alcohols, such as xylitol, can also lend flexibility to PEDOT/PSS, which could pioneer new applications of the organic electrodes. We believe that these conductive binders and modified separators could contribute to the development of organic secondary batteries that display high energy densities per electrode, excellent cyclability, and flexibility.

It should be noted that PEDOT/PSS electrode fabrication can be easily reproduced in a university lab on a smaller scale without using mixing machinery; one batch for tens of coin cells needs only a small amount of organic active materials (40 mg). When a precious organic compound is newly synthesized, its potential performance as a battery can be confirmed with a very small amount of the compound.

### Table 3. Assumed Conditions and Energy Densities of the Various Electrodes

| Electrode Type | Active Material (mg [wt %]) | Electrode with Organic Active Materials (Proposed Method) | Electrode with Inorganic Active Materials (Lithium Iron Phosphate) | Electrode with Inorganic Active Materials (Lithium Cobalt Oxide) |
|----------------|-----------------------------|-------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| PEDOT-type (in slurry) | 41.4 [61] | 23.5 [34] | 3.4 [5] | 3.8 |
| PTFE-type (for coin-type cells) | 11.9 [39] | 15.4 [51] | 3.1 [10] |
| PVdF-type (in slurry) | 80.3 [80] | 2.1 [10] | 2.1 [10] | 50.3 [5] |

### Table 4. Weight and Ratio of Each Mixed Material When Preparing the PEDOT-Type Electrode in Slurry, the PTFE-Type Electrode for Four Coin-Type Cells, and the PVdF-Type Electrode in Slurry

| Electrode Type | Active Material (mg [wt %]) | PEDOT/PSS (mg [wt %]) | D-sorbitol (mg [wt %]) | AB (mg [wt %]) | PTFE (mg [wt %]) | PVdF (mg [wt %]) |
|----------------|-----------------------------|-----------------------|-----------------------|--------------|----------------|----------------|
| PEDOT-type (in slurry) | 41.4 [61] | 23.5 [34] | 3.4 [5] | 3.8 |
| PTFE-type (for coin-type cells) | 11.9 [39] | 15.4 [51] | 3.1 [10] |
| PVdF-type (in slurry) | 80.3 [80] | 2.1 [10] | 2.1 [10] | 50.3 [5] |

### CONCLUSIONS

This study investigated the effect of PEDOT/PSS with D-sorbitol as a conductive binder and as a separator modifier and used indigo as a model electrode active material. Varying the content of active material in the electrode from 40 to 90 wt %, we compared the discharge capacities of the cells using three binders, PEDOT/PSS, PVdF, and PTFE. With 80 wt % of active material in the electrode, the PEDOT/PSS and PVdF binder extracted, respectively, 96 and 73% of the theoretical capacity of indigo, whereas the capacity was minuscule when PTFE was used. The high capacity per net electrode weight was achieved using PEDOT/PSS and D-sorbitol as a conductive additive. In addition, coating the separator with PEDOT/PSS and D-sorbitol increased the cycle life.

The present method proved that a conductive polymer binder can increase the energy density of the organic electrode to an extent that rivals the current inorganic electrodes, thereby paving the way for flexible rare-metal-free batteries.

### EXPERIMENTAL METHODS

**Materials.** Indigo (97%) and D-sorbitol (>97%) were purchased from Tokyo Chemical Industry, Japan. An aqueous solution containing 0.5 wt % PEDOT and 0.8 wt % PSS solution was purchased from Sigma-Aldrich, Japan. The electrolyte solution was prepared by dissolving 2.5 mol L⁻¹ of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Kishida Chemical, Japan, 99.9%) in propylene carbonate (Kishida Chemical, Japan, >99.5%).

**Electrode Preparation.** PEDOT-Type Electrode. The electrodes were prepared by following the method described in our previous report. Indigo (the active material) in a powder state was mixed with a PEDOT/PSS solution and D-sorbitol at the solid-weight ratios of 61:34:5 (labeled as [60 wt %-indigo/PEDOT]), 70:27:3 ([70 wt %-indigo/PEDOT]), 79:18:3 ([80 wt %-indigo/PEDOT]), and 85:12:3 ([85 wt %-indigo/PEDOT]), as summarized in Table 4. Ethylene glycol, at volumes in the range of 20–26 mg, was also added to
the mixture, which was then sonicated for 50 min and moderately heated on a hot plate at approximately 110 °C, where the D-sorbitol melted and the water evaporated such that the viscosity of the slurry became appropriate for coating. The resulting slurry was coated on an aluminum-foil current collector using a film applicator (a doctor blade) with a gap of 150 μm and sequentially dried at 80 °C for 1 h and then at 100 °C for 2 h under vacuum conditions.

For comparison, a slurry and the resulting electrode without D-sorbitol were also produced (Figure S1). Without the addition of D-sorbitol, a part of the coated slurry film peeled from the current collector after drying. With D-sorbitol in the mixture, the peeling was not observed. Thus, the addition of D-sorbitol was confirmed to improve the adhesion of the PEDOT/PSS electrode with the current collector. The resulting electrode was punched into a disk shape (Ø 14 mm).

**PTFE-Type Electrode.** Indigo, acetylene black (AB; a conductive additive), and PTFE (a binder) were mixed at solid-weight ratios of 39:51:10 (labeled as [40 wt %-indigo/PTFE]), 59:30:11 (60 wt %-indigo/PTFE), and 80:10:10 (80 wt %-indigo/PTFE) using a mortar and pestle (Table 4). The composite was pressed onto an Al mesh (Ø 14 mm) and dried at 120 °C under vacuum conditions for 1 h.

**PVdF-Type Electrode.** Indigo and AB were added to a solution of PVdF (a binder) in NMP to produce a slurry with a gap of 150 μm and sequentially dried at 80 °C for 1 h and then at 100 °C for 2 h under vacuum conditions. The resulting electrode was punched into a disk shape (Ø 14 mm).

**Separator Modification. Polymer-Coated Separator.** PEDOT/PSS solution and D-sorbitol were mixed at a PEDOT/PSS solution/D-sorbitol weight ratio of 250:1. The conductive polymer-coated separator was prepared by dropping approximately 300 μL of mixed solution onto one side of a glass filter (Ø 16 mm, 0.44 mm-thick, GA-100, Toyo Roshi Kaisha, Japan), followed by drying at 120 °C for 1 h; the coated separator was then dried again at 100 °C for 2 h under vacuum conditions.

**FE-SEM Observation.** A field emission scanning electron microscope (FE-SEM, JSM-6700FV, JEOL, Japan) was used to observe the electrodes before cell assembly. The cross sections were polished by an Ar-ion beam after cutting the electrodes with scissors prior to imaging.

**Cell Assembly.** Coin-type cells were assembled to evaluate the battery performance of the electrodes with and without polymer-coated separator. The prepared electrode, separator (glass filter, or polymer-coated separator, Ø 16 mm), electrolyte, and lithium-metal negative electrodes were placed in an IEC R2032 coin-type cell in a dry chamber (dew point < -60 °C).

**Battery Testing.** The cells were galvanostatically charged and discharged at 25 °C at a current density of 20 mA g\(^{-1}\) in the voltage window of 1.5−3.0 or 1.5−3.5 V using a battery evaluation system (BLS series, Keisokuki Center, Japan). The cycle was initiated by discharging, during which the active material was lithiated (Li\(^+\) ions were inserted). The current density, 20 mA g\(^{-1}\), corresponded to a C-rate of 0.098 based on the theoretical capacity of indigo (204 mAh g\(^{-1}\), under the assumption of a two-electron transfer per molecule process).

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# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00313.

Optical images of the surface of a PEDOT-type electrode with and without D-sorbitol (Figure S1); theoretical redox reaction and charge and discharge curves and cycle trend for 1,1′-iminodianthraquinone (IDAQ) (Figure S2); and their electrode composition (Table S1) (PDF)

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## Author Contributions

M.K. conceived of the presented idea and planned the experiments. M.K. and H.S. carried out the experiment. M.K., H.S., M.Y., and T.K. contributed to the interpretation of the results. N.T. helped supervise the study. M.K. and H.S. wrote the manuscript with support from T.K. and M.Y. All authors approved the manuscript to be published.

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## Notes

The authors declare no competing financial interest.

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