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## A New Bio-based Battery Material: Effect of Rate of Anthraquinone Skeleton Incorporation into Polyglycidol on Battery Performance

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### Abstract

A new battery material that is composed of polyglycidol and a redox-active anthraquinone unit (AQ) was prepared and was then used as a positive electrode for lithium ion batteries. Polyglycidol (pGD) is a bio-based polymer that is derived from the waste glycerin that is discarded during bio-diesel processing. The pGD-AQ electrode has a potential plateau at 2.3 V vs. Li<sup>+</sup>/Li, and a discharge potential that decreased gradually with a capacity of 139 mAh g<sup>-1</sup>. The cycle-life stability of pGD-AQ is better than that of chloroanthraquinone, which was used as a reference material. A higher AQ skeleton incorporation rate into pGD leads to a higher battery capacity. These results show that the incorporation of the AQ unit into the polymer is an effective way to improve battery performance in terms of both capacity and cycle-life stability.

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## 1. Introduction

The demand for rechargeable lithium ion batteries is increasing with the widespread use of portable electronic devices. Current lithium ion batteries contain minor metals such as cobalt and nickel in their positive electrodes. From the perspectives of both resource availability and cost problems, alternative material options to replace these minor metals are strongly desired. The use of redox-active organic materials for the positive electrode is one promising way to overcome these problems [1–3].

In our previous study, we reported the use of quinone-based materials as minor metal-free positive electrodes that can lead to high discharge capacities because of their multi-electron redox properties [4–7]. Several low-molecular-weight quinone-based materials, including benzoquinone, anthraquinone and pentacenetrone, were studied, and it was found that their discharge capacities tended to decrease upon cycling [5–7]. The main cause of these falls in capacity is considered to be dissolution of the active material in the electrolyte solution.

Incorporation of the redox active unit into the insoluble polymer matrix is one approach that has been used to improve the cycling stability of organic active materials. For example, a polyacrylate-based active material that shows relatively high capacity and good cycling stability has been reported in the literature [8].

Another approach that is currently under study involves the use of bio-based products as raw materials. The utilization of naturally-derived compounds can also reduce the resource risks caused by a dependence on petroleum.

In this study, we report on the synthesis and the battery performance of a new electrode material composed of polyglycidol and anthraquinone. Polyglycidol is one of the bio-based polymer materials that can be prepared from the waste glycerin that is discarded during bio-diesel processing. The effects of incorporation of the active material into the polymer matrix on the battery performance are also discussed.

## 2. Experimental

### 2.1. Materials

All chemicals and solvents used were of the highest grade obtainable, and were used without any further purification. 2-Chloroanthraquinone (Cl-AQ) and 1-methyl-2-pyrrolidone (NMP) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Magnesium ethoxide, tetraphenyl tin, tin(II) 2-ethylhexanoate, and dimethyl sulfoxide (DMSO) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI),  $\gamma$ -butyrolactone (GBL) and triethylene glycol dimethyl ether (3EG) were obtained from Kishida Chemical Co., Ltd. (Osaka, Japan).

### 2.2. Synthesis of polyglycidol (Scheme 1, step 1)

Polyglycidol (pGD) was prepared via the ring-opening reaction of glycidol (Wako Pure Chemical Industries, Ltd., Japan) using a catalyst. In a typical experiment, a mixture of glycidol (20 g) and the catalyst (1 mol%) was placed in a round-bottomed flask equipped with a condenser. The mixture was then heated in an oil bath while stirring for one week. The reaction mixture was cooled to room temperature and was then dissolved in methanol before being reprecipitated using acetonitrile to give the crude polymeric product. The crude product was then washed three times with acetonitrile and was dried at 50°C under reduced pressure conditions.

### 2.3. Synthesis of active materials (Scheme 1, steps 2 and 3)

The anthraquinone unit was incorporated into pGD by following the Williamson synthesis procedure. In a typical experiment, pGD and sodium metal were placed into a round-bottomed flask with a solvent, and the mixture was stirred continuously at room temperature until no hydrogen gas was evolved. The solution became dark brown in color with increasing time on-stream, and then Cl-AQ was added, before the resulting mixture was stirred for 5 h. The crude mixture was purified by washing three times with an appropriate solvent. The target product was finally obtained after drying under reduced pressure at 100°C for 3 h.

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