

High-Capacity Lithium Polymer Batteries Prepared by Ceramic Electrolyte Coating LiCoO₂

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INTRODUCTION

A solvent-free lithium polymer battery is suitable for a stationary-use large-scale battery system from the viewpoint of high energy density with ultimate safety. Although the polymer electrolyte was oxidized at high potential (*e.g.*, >4 V), we could prepare 5 V class polymer batteries by ceramic electrolyte coating a thin-film cathode (LiNi_{0.5}Mn_{1.5}O₄) surface [1]. In this system, which was named the “ceramic / polymer composite electrolyte”, the oxidative degradation of the polymer electrolyte was prevented by the ceramic electrolyte. Furthermore, a high-capacity polymer battery has been prepared using this concept, in which LiCoO₂ showed reversibility up to 4.6 V with a discharge capacity of more than 200 mAhg⁻¹ at the 1st cycle [2]. The sheathing material was Li₃PO₄ because of the easy preparation of a thin film on the cathode. However, it is a relatively poor ionic conductor ($\log\sigma_{RT}=-8$), thus the substitution of Li₃PO₄ is required from a practical viewpoint. In this work, a novel lithium ionic conductor with a NASICON structure, LiAl_{0.5}Ge_{1.5}(PO₄)₃ (LAGP), was used as a coating ceramic electrolyte. The high ionic conductivity of LAGP ($\log\sigma_{RT}=-4$) was reported by Yamamoto *et. al.*, [3].

EXPERIMENTAL

LAGP was prepared by heating a stoichiometric mixture of LiOH·H₂O, Al(NO₃)₃·9H₂O, GeO₂, and (NH₄)₂HPO₄ at 1173 K for 20 h. LAGP-coated LiCoO₂ (weight ratio: LAGP / LiCoO₂= 1 / 20) was obtained using a hybridization system (Nara Machinery, NHS-0). A positive electrode sheet was prepared using the mixture of coated LiCoO₂, acetylene black, and the polymer electrolyte. Lithium bis(pentafluoroethylsufonyl)amide (LiBETI) was dissolved in a polymer electrolyte, ethylene oxide co-2-(2-methoxy-ethoxy) ethyl glycidyl ether, [P(EO/MEEGE)] (Daiso Co., Ltd.). The matrix polymer sheet (SPE) was P(EO/MEEGE/AGE) (AGE: allyl glycidyl ether). The dissolved salt in the matrix polymer was lithium tetrafluoroborate (LiBF₄). The ionic conductivities of the LAGP pellet and the matrix polymer sheet are measured using an AC impedance technique. The coin-type cell (CR2032), consisting of [LAGP-coated LiCoO₂ | SPE | Li], was set up in an Ar-filled glove box. The cell was operated between 3.0 and 4.4 V at 333 K. The applied current was 100 μAcm⁻², which corresponded to a rate of C/8.

RESULT AND DISCUSSION

The obtained LAGP was confirmed by XRD, and coexisted the trace impurities of Li₄P₂O₇, GeO₂ and AlPO₄. The ionic conductivities of LAGP and SPE are shown in Fig. 1. Both electrolytes showed *c a.* 5×10⁻⁴ Scm⁻¹ at 333 K and similar characteristics to those previously reported [3].

The cycle characteristics of [LAGP-coated LiCoO₂ | SPE | Li] and [non coated LiCoO₂ | SPE | Li] cells are shown in Fig. 2. The initial discharge capacity of the LAGP-coated cell, in which the calculated weight of the active material included the weight of coated LAGP, was 186 mAhg⁻¹. The reversibility of Li_{1-x}CoO₂ was more than *x*=0.65 at the charge cutoff voltage of 4.4 V in this system. The relative capacity maintained 80 % of the initial capacity at 40th cycle. On the other hand, the discharge capacity of non coated LiCoO₂ rapidly decreased within 10 cycles. Seki *et. al.*, reported that the impedance at the LiCoO₂ / SPE interface markedly increased more than at 4.2 V [4]. Therefore, LAGP serves partly as an oxidation barrier for the SPE at a high-potential region, and also as a lithium ionic conductor between LiCoO₂ and the SPE. Furthermore, the operation current density of the LAGP-coated system (100 μAcm⁻²) was twice larger than that of the Li₃PO₄-coated system (50 μAcm⁻²) [2]. The high ionic conductivity of LAGP improves the rate capability of the cell. Thus, this ceramic / polymer composite electrolyte concept reveals the possibility of realizing a high-capacity and high-voltage battery system with sufficient safety.

