



Electrochemical properties of LiCoPO_4 -thin film electrodes in LiF-based electrolyte solution with anion receptors



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HIGHLIGHTS

- Electrochemical properties of LiCoPO_4 thin-film electrodes were investigated.
- LiF-based electrolyte solutions containing anion receptors were used.
- Electrochemical properties of LiCoPO_4 were depended on the kind of anion receptors.

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ABSTRACT

Compatibility of LiF + anion receptors/propylene carbonate (PC) electrolyte solution with high potential positive electrode for lithium-ion batteries was examined by cyclic voltammetry. As anion receptors, tripropyl borate (TPB), tris(pentafluorophenyl) borane (TPFPB), and tris(hexafluoroisopropyl) borate (THFIPB) were used. LiCoPO_4 thin-film electrodes were prepared by sol–gel method and used as both carbon- and binder-free model electrodes. From cyclic voltammograms, LiCoPO_4 showed better cycleability in $0.1 \text{ mol dm}^{-3} \text{ LiF} + 0.1 \text{ mol dm}^{-3} \text{ THFIPB/PC}$, however, other anion receptors did not give positive influence. It is indicated that the surface protecting layer from F^- -THFIPB complex and made LiCoPO_4 stable. Electrochemical behavior depending on anion receptors was discussed according to reaction activity of F^- .

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1. Introduction

Recently, lithium-ion batteries (LIB) have been paid much attention as the power sources of the electric vehicles (EV), the plug-in hybrid electric vehicles (PHEV), and the hybrid electric vehicles (HEV) [1–3]. For the application of LIBs to various EVs use, higher energy densities compared with present LIBs are required. In order to obtain high energy densities, the increase of the capacity or the working voltage should be achieved. From the view of the reaction mechanism known as topo-chemical reaction in LIBs, large increase of capacity is not easy due to the limited lithium insertion/extraction sites in host materials. The working voltage has been limited by the electrochemical window of electrolyte solutions. Therefore the high potential positive electrode materials (near 5 V vs. Li/Li^+) have not been put to practical use yet and electrolyte solutions with wide electrochemical window should be developed.

Inorganic lithium salt-based electrolyte solutions for LIBs have been developed by Brookhaven National Lab [4–9]. As inorganic lithium salts, LiF, Li_2O , and so on have been reported. These inorganic lithium salt are composed of hard Lewis acid (Li^+) and hard Lewis base (F^- or O^{2-}), therefore, the ionic bond is quite strong and they are hard to dissolve in organic solvent. In order to dissolve inorganic lithium salts in organic solvent, anion receptors that are stronger Lewis acid than Li^+ were added. Since anion receptor forms donor–acceptor interaction with F^- , not only solubility of inorganic lithium salts increases but also F^- is trapped in electrolyte solution and large Li^+ transportation number is obtained. In these electrolyte solutions, the oxidative reaction of anion can be suppressed due to the high redox potential of anion and high oxidation stability was reported [4–9]. Therefore, these electrolyte solutions are attractive as new electrolyte solutions for high voltage LIBs.

Fluorine (F) or fluoride (F^-) is one of the key factors to form stable interface between positive electrode and electrolyte solution. In the LiF-based electrolyte solution, cycleability of LiMn_2O_4 was reported to be enhanced compared with LiPF_6 -based electrolyte solution at elevated temperature [4]. Also, it was reported that

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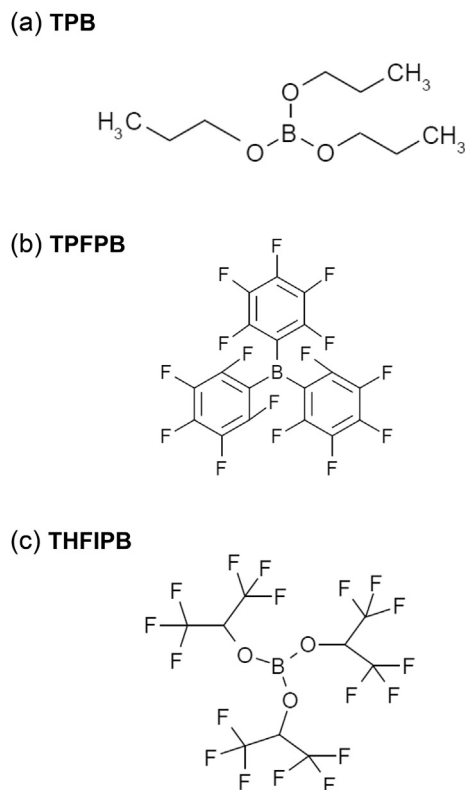


Fig. 1. Molecular structures of anion receptors. (a) TPB, (b) TPFPB, and (c) THFIPB.

surface fluorination of LiMn_2O_4 increased cycleability by introduced F [10]. Based on these reports, it is considered that F or F^- plays an important role in the positive electrode reaction. In other words, control of reaction activity of F or F^- must be important. In the LiF-based electrolyte solutions, the reaction activity of F^- is supposed to be depended on the interaction with anion receptor. Fortunately, this interaction can be controlled by Lewis acidity of anion receptor. Although effect of anion receptor additives in LiPF_6 -based electrolyte solution on electrochemical performance of LIBs

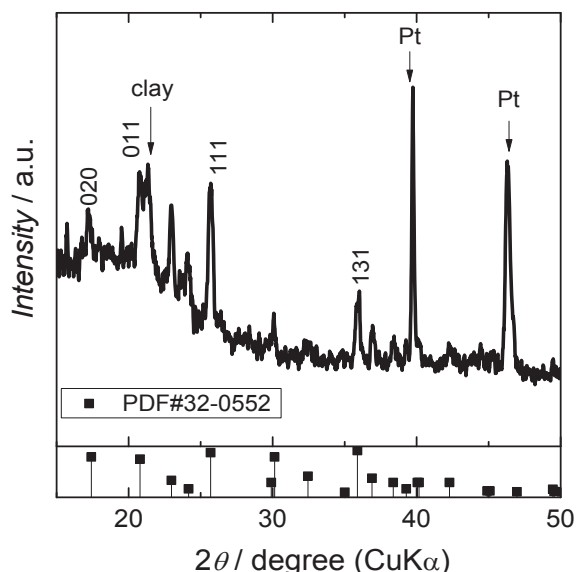


Fig. 2. XRD pattern of LiCoPO_4 thin-film electrode.

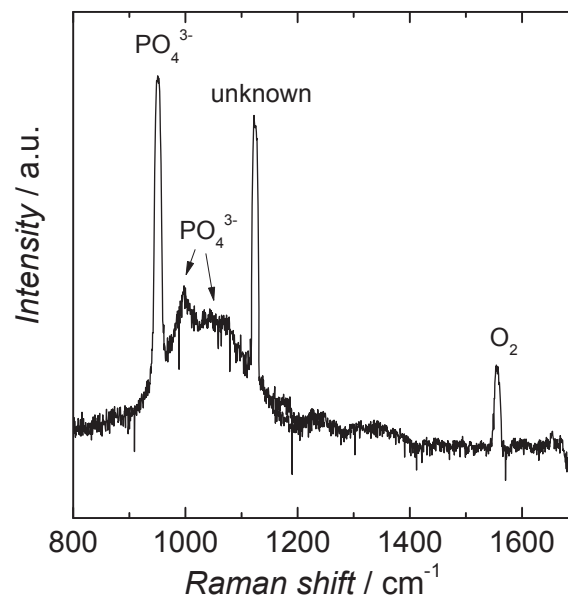


Fig. 3. Raman spectrum of LiCoPO_4 thin-film electrode.

was reported [11], there is no report that focused on the reaction activity of F^- at positive electrode reaction.

In this study, we focused on the reaction activity of F^- and electrochemical properties of LiCoPO_4 in LiF-based electrolyte solutions containing anion receptor were investigated. LiCoPO_4 is attractive 5 V-class positive electrode materials, because of the high working potential of 4.8 V vs. Li/Li^+ , high theoretical capacity (167 mA h g^{-1}), and thermal stability by the strong covalent bonds between oxygen ions and the P^{5+} in PO_4^{3-} tetrahedral polyanions [12–22]. However, due to the high working voltage, cycleability of LiCoPO_4 in common ester based electrolyte solutions is not high. As mentioned above, F^- plays important role in the positive electrode reaction. Hence we tried to control the reaction activity of F^- and enable LiCoPO_4 to work successfully. We choose the thin-film form of LiCoPO_4 and investigated the electrochemical properties of LiCoPO_4 thin-film electrodes in LiF-based electrolyte solution with anion receptors.

2. Experimental

A LiCoPO_4 thin-film electrode was prepared by a sol-gel method. Stoichiometric amount of lithium acetate, cobalt (II) acetate tetrahydrate and ammonium dihydrogenphosphate were dissolved in citric acid aqueous solution. After adding methanol, polyvinylpyrrolidone ($M_w = 55,000$) was added to the solution and transparent solution was obtained. The obtained solution was coated on the platinum substrate by spin-coating (3500 rpm, 30 s). The obtained gel film was heated at 700°C for 3 h under the air in order to synthesis LiCoPO_4 thin-film electrodes.

Scanning electron microscope (SEM) observation was conducted by using S3000-H (HITACHI) to examine the film thickness. X-ray diffraction (XRD) measurement was carried out by using Rint-2500 (RIGAKU) for the identification of resulting thin-film electrodes. Raman spectroscopy (Jobin-Yvon; T-64000) was used as the surface characterization of resulting thin-film electrodes. Surface chemical analysis was carried out by using X-ray photoelectron spectroscopy (XPS, ULVAC-Phi; MT-5500).

A three-electrode cell was used for electrochemical measurement. A resulting thin-film electrode was used as a working electrode and lithium foils are used as a counter electrode and a

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