別紙４（課程博士）

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Abstract

論文内容の要旨　（博士）

Title of Thesis 博士学位論文名	Design of microstructure in electrochemical devices by electrophoretic deposition for their performance improvement (電気泳動堆積法による電化学素子の微構造設計と特性向上)

(Approx. 800 words)

(要旨　1,200 字程度)

Electrophoretic deposition (EPD) is an important technology for colloidal coating processes. A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in electrophoretic deposition. This includes materials such as polymers, pigments, dyes, ceramics, and metals. Compared to other advanced coating techniques, the EPD process is very versatile since it can be modified easily for a specific application. For instance, materials with varied structure such as nanoscale assembly, micro patterned thin films, laminated or graded materials, hybrid materials, particle-reinforced materials, etc. can be prepared by adjusting conditions of EPD.

On the other hand, recently, electrochemical devices, which can convert electrical energy and chemical energy reversibly, have attracted much interest as promising power sources for the next generation. In these devices, various functional materials are employed according to the working principle of electrochemical devices, and their performances are dependent considerably on the nano- to microscale structure of the functional materials. Hence, studies on how to fabricate electrochemical devices with optimum structure, using different kinds of functional materials to obtain devices of high performance are essential. Thus, the EPD technique, which can easily control nano- and microstructure of materials, is a suitable process for the novel preparation of electrochemical devices with expected enhanced performance.

In this work, applications of EPD in the preparation of electrochemical devices, mainly photoelectrochemical cells and all-solid-state lithium ion batteries, is explored. According to our results obtained, electrochemical devices fabricated by the EPD technique show a potential of practical applicability of these devices with more improvement in the EPD procedure used.

The automatic multilayer coating system used in this work, based on electrophoretic deposition process, which includes coating, drying, and washing, are proposed for stable and effective preparation of multilayered films. Multilayered structures are one of the target structures in the fabrication of functional materials by EPD because they are favorable for significantly enhancing the properties of electrochemical devices and for device

integration. As demonstration of the system, multilayered films consisting of layers of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) and Al_2O_3 particles were fabricated under constant applied voltage and current. Results indicate that the film structures, such as the thicknesses of the inner layers and number of layers are controllable by varying conditions of processes flow in a simple operation. The EPD system is also expected to be applied for the preparation of particle-reinforced composite materials, which have been attempted in this work too.

As study case of performance evaluation of functional film with controlled nanostructure, the composite films of NiTi-layered double hydroxide (NiTi-LDH, $[Ni_{1-x}Ti_x(OH)_2]^{2x+}(A^{n-})_{2x/n}\cdot mH_2O]$) with various contents of reduced graphene oxide (rGO) were prepared by the EPD; these composites were employed as a visible-light responsive photoanode in photoelectrochemical cells based on Honda-Fujishima effect. The approximately 10 μm-thick NiTi-LDH/rGO films were deposited on fluorine-doped tin oxide (FTO) glass. The rGO containing films of NiTi-LDH/rGO|FTO showed a higher photovoltage than the film without rGO of NiTi-LDH|FTO. Electrokinetic parameters, especially photogeneration rate and chemical capacitance, were significantly affected by increasing Ti^{3+} surface defects due to the hybridization with rGO. The increase in these two parameters predominately contributed to the enhancement of the photovoltage. The expected effects due to the nanocomposite structure were also observed substantially in the performance of the composites-based EPD films employed as photoanode, which showed highly sensitive in both their nanoscale and microscale structures.

EPD technique was also employed in the preparation of effective solid-state electrolyte layer, based on Li_2S-P_2S_5 (LPS) which is a promising key functional material in all-solid-state lithium ion batteries. A suspension of LPS precursor, prepared by liquid shaking (LS) method, was employed in this EPD processing, as novel colloidal coating technique. LS method has been reported in our previous study as a novel method of synthesis of LPS. LPS is not stable in polar solvents, which are the common solvents used in EPD. However, an LPS precursor deposited film was obtained successfully from its precursor suspension in a non-polar solvent because of its positive surface charge. Homogeneous film thicknesses of 10~100 μm were controllably prepared. An EPD deposited precursor film of LPS, aged by warm pressing, exhibited high conductivity (1.98×10^{-4} S cm^{-1}), at ambient temperature, and significantly low activation energy (16.6 kJ mol^{-1}), compared with conventional LPS materials. Thus, good solid-solid interfacial contact can be obtained in the sulfide-based ionic conductor by employing EPD process followed by warm pressing.

For application as a cathode in all-solid-state lithium ion batteries, films with ordered multilayer structure of NMC and LPS were fabricated by alternate EPD process using the automatic EPD system, LS method, and novel dispersant for NMC. The specific structure, thickness, and number of layers were controllable by adjusting various conditions in the EPD process. Employing the multilayer film as cathode, the single battery cell exhibited typical charge/discharge behaviors with cell capacity of approximately 25 mAh g^{-1}. In order to achieve a practically applicable cathode, the film structures should be optimized by adjusting for optimal conditions in the EPD process.