論文 / 著書情報
Article / Book Information

題目(和文)	カーボンナノ材料用分散剤を目的としたポリアクリル酸誘導体の分子設計
Title(English)	Molecular Design of Poly(acrylic acid) Derivatives for Dispersant of Carbon Nanomaterials
著者(和文)	久保寺茜
Author(English)	Akane Kubotera
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10118号, 授与年月日:2016年3月26日, 学位の種別:課程博士, 審査員:斎藤 礼子,高田 十志和,芹澤 武,大塚 英幸,小西 玄一
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10118号, Conferred date:2016/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Thesis Outline

"Molecular Design of Poly(acrylic acid) Derivatives for Dispersant of Carbon Nanomaterials"

Chapter 1 Introduction

Anode of lithium ion battery (LIB) consists of an active material, a collector, a conductive additive, a binder and so on. Carbon nanomaterials, which are used as the active material and the conductive additive, are easy to aggregate. Thus, dispersant is usually added to the electrode. Polymer dispersants are effective due to large steric hindrance. Poly(acrylic acid) (PAA) is used as an anionic dispersant. PAA has been reported as the good anode binder of LIB. The conventional anode binder is poly(vinylidene difluoride) (PVDF). 1-Methyl-2-pyrrolidone (NMP) is usually used as the solvent. In the case of PAA binder, water can be used as the solvent instead of NMP. The initial discharge capacity and cycle repeatability of the LIB with PAA binder are higher than that with PVDF binder. In the thesis, the effect of the polymer architecture and the presence of hydrophobic sequence on the dispersion of the carbon nanomaterials was investigated to produce PAA derivative dispersants with the function of the binder.

Chapter 2 Synthesis and properties of 3arm and 6arm poly(acrylic acid)s and their derivatives

3arm and 6arm PAAs were synthesized via atom transfer radical polymerization (ATRP) of methyl acrylate subsequent hydrolysis. 3arm and 6arm poly(methyl acrylate)s were synthesized using 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene and hexakis(bromomethyl) benzene as initiators to prevent the decomposition caused by hydrolysis. In spite of steric hindrance caused by locally concentrated reaction groups of the initiator, the polymers with well-defined arm number were synthesized by feed control, additional molar catalyst and ligand to the reaction groups of the initiators. The degrees of hydrolysis of the star polymers did not reach 100 %, however, the solubility and thermal decomposition behavior of the polymers were similar to those of linear PAA. In addition to the 3arm and 6arm PAAs, 6arm PAAs with hydrophobic sequence were synthesized.

Chapter 3 Synthesis of poly(acrylic acid)-poly(amideimide) copolymers

Hydrophobic poly(amideimide) (PAI) has good affinity with carbon nanomaterials. Poly(acrylic acid)-*block*-poly(amideimide) (PAA-PAI), poly(acrylic acid)-*block*-poly(amideimide)-*block*-poly(acrylic acid) (PAA-PAI-PAA), and hetero-arm poly(acrylic acid)$_2$poly(amideimide) (PAA_2PAI) were synthesized. Three architectural copolymers with similar molecular weights and PAA contents were synthesized by the capping or modification with an azoinitiator of the ends of PAI sequence subsequent polymerization of acrylic acid.

Chapter 4 Dispersion carbon nanoparticles with the poly(acrylic acid) derivatives

Dispersion of Ketjen black (KB) by the poly(acrylic acid) derivatives was investigated in NMP and water by ζ-potential measurement, dynamic light scattering measurement (DLS), UV-vis spectroscopy, and transmission electron microscopy (TEM). The dispersibility of the poly(acrylic acid)-poly(amideimide) copolymers, especially that of PAA_2PAI was higher than that of the other polymers. The attachment of PAI sequence to KB was observed by TEM. The dispersibility of 3arm and 6arm polymers with hydrophobic sequence was better than that of linear PAA in NMP.

Chapter 5 Dispersion of carbon nanotube in water with the poly(acrylic acid) derivatives

Dispersion of carbon nanotube (CNT) was investigated in water. The dispersibility of the poly(acrylic acid)-poly(amideimide) copolymers, especially that of PAA_2PAI was higher than that of the other polymers as well as the dispersion of KB. The dispersibility of PAA-*block*-PAI-*block*-PAA was more effective for the dispersion of CNT that that of PAA-*block*-PAI. TEM image indicated that the mixture of PAA_2PAI and CNT formed nanoparticles with networks.

Chapter 6 Battery properties of the cells with the poly(acrylic acid) derivatives

The battery properties of the LIBs with 3arm and 6arm PAAs, poly(acrylic acid)-poly(amideimide) copolymers, and 6arm poly(acrylic acid)-*block*-polystyrene binders were investigated. The initial discharge capacity and the initial inner resistance drop of the LIBs with 3arm and 6arm PAA binders were better than those with linear PAA binder. Cycle repeatability of the LIBs with 3arm and 6arm PAA binders was also good. Architecture is important for the battery properties. The initial discharge capacity and the initial inner resistance drop of the LIBs with poly(acrylic acid)-poly(amideimide) copolymers were worse than those with linear PAA.

Chapter 7 Conclusions

Architecture of the star polymers and the presence of the hydrophobic sequence were important for the PAA derivative dispersants. PAI sequence was especially effective for dispersion of carbon nanomaterials in water.