

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Development of Novel Preparation Methods of Silica Anode Material for Lithium-ion Batteries
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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10030号, 授与年月日:2015年12月31日, 学位の種別:課程博士, 審査員:谷口 泉,伊東 章,久保内 昌敏,多湖 輝興,篠崎 和夫
Citation(English)	Degree:., Conferring organization: Tokyo Institute of Technology, Report number:甲第10030号, Conferred date:2015/12/31, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
Doctoral Program

論文要旨

THESIS SUMMARY

専攻 : Department of	Chemical Engineering	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 Doctor of	(Engineering)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Novel preparation methods of SiO₂/C nanocomposite and nano-SiO₂/C composite anode materials for lithium-ion batteries were developed by utilizing mechanochemical assisted sol-gel, drip combustion in a fluidized bed reactor, and ultrasonic spray pyrolysis methods combined with a dry ball milling process. In Chapter 1, a general overview on the lithium-ion battery technology and recent research advances in anode materials were provided. A detailed literature review was devoted to silicon oxide (SiO_x) (0 < x ≤ 2) anode materials and their preparation methods. Great perspectives of SiO₂/Carbon (C) composite as a next-generation anode material were highlighted and relevant literature on problems and attempted solutions for its practical application were reviewed. Finally the objectives of this study were introduced. In Chapter 2, SiO₂/C nanocomposites were successfully prepared by a combination of mechanochemical-assisted sol-gel and dry ball milling (DBM) processes. In this preparation method, the mechanical energy from ZrO₂ balls in the high energy ball milling procedure was utilized to hydrolyze tetraethyl orthosilicate (TEOS) in the presence of a catalyst (HNO₃ or NH₄OH) and acetylene black. Since this synthesis method yields hardly agglomerated SiO₂/C composite with a particle size of 100 μm orders and a poor distribution of carbon and SiO₂, DBM was introduced into the synthesis pathway to obtain SiO₂/C nanocomposites consisting of highly dispersed carbon nanoparticles on fine amorphous SiO₂ particles. As a result, the SiO₂/C nanocomposite prepared using HNO₃ catalyst, heat treatment at 600 °C in a N₂ atmosphere and optimized DBM process exhibited a highly stable reversible capacity of 663 mAh g⁻¹ (872 mAh g-SiO₂⁻¹) with an initial Coulombic efficiency of 53% at a current density of 46 mA g⁻¹ after 30 cycles with no capacity fading. This sample contained SiO₂/C agglomerates of ~2 μm in size. Further attempt to decrease the particle size and improve the electrical properties of the SiO₂/C nanocomposite involved some modifications of the synthesis route through the employment of an ammonia catalyst, a polyvinylpyrrolidone (PVP) dispersing agent and heat treatment at 900 °C in a N₂ + 3% H₂ atmosphere. The obtained material exhibited the initial charge capacity of 760 mAh g⁻¹ (1121 mAh g-SiO₂⁻¹) and Coulombic efficiency of 54% with a slight capacity fading over 25 cycles at a current density of 50 mA g⁻¹. However, the introduced modifications afforded a decrease of SiO₂ particles size to a few hundreds of nanometer, which presumably restricts access to full lithium storage capacity of SiO₂ anode. In Chapter 3, nano-SiO₂/C composites were successfully prepared by the drip combustion in a fluidized bed reactor. Kerosene was employed as a solvent and carbon source in the precursor solution. A solid particle formation mechanism in this process afforded nano-SiO₂/C composites containing nano-agglomerates with hierarchical fractal morphology and SiO₂ primary particles of approximately 50 nm in size. However, the as-prepared material exhibited an initial charge capacity of 319 mAh g⁻¹ at current density of 50 mA g⁻¹ over a voltage range from 0.01 to 3.0 V versus Li/Li⁺. After annealing at 900 °C in a N₂+3% H₂ atmosphere and high-energy DBM process, the obtained dry-milled nano-SiO₂/C composite showed a markedly improved electrochemical performance with an initial charge capacity of 533 mAh g⁻¹ and Coulombic efficiency of 46%. The findings obtained throughout this study suggest that high carbon contents in the sample prepared by the drip combustion in a fluidized bed reactor impeded the mixing and dispersing efficiency of the DBM process. As a result, a poor distribution between nanostructured SiO₂ and carbon inhibited the electrochemical properties of the nano-SiO₂/C composite. In Chapter 4, SiO₂/C nanocomposites were successfully synthesized through the combination of SP synthesis method with DBM process. Sucrose was introduced as a carbon source into the precursor solution of SP. Physical characterization of as-prepared samples revealed that SP synthesis affords dense amorphous SiO₂/C microparticles (~1 μm) of spherical shape with a narrow particle size distribution. Moreover, a careful inspection of the cross-section of the sample by SEM-EDS analysis showed that sucrose additive facilitates a homogeneous distribution of carbon at a molecular level inside SiO₂ microparticles. A DBM process was employed to downsize micro-sized particles to nanometer scale (~100 nm), and uniformly disperse these particles in AB matrix. The final SiO₂/C nanocomposite prepared with 0.1 mol L⁻¹ sucrose concentration exhibited an initial charge capacity of 848 mAh g⁻¹ (1344 mAh g SiO₂⁻¹) with a Coulombic efficiency of 60% at a current density of 50 mA g⁻¹ in the voltage range between 0.01 and 3.0 V. A slight capacity decay observed over 20 cycles was attributed to the mechanical destruction of the electrode caused by volume variations of Si during lithium-ion insertion and extraction processes. The outstanding lithium-storage properties of the prepared material are attributed to the SP synthesis method. In Chapter 5, conclusions were presented based on the above mentioned summarized results.