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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 (Engineering) Doctor of
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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

Novel preparation methods of SiO_2/C nanocomposite and nano-SiO_2/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) ($0 < x \leq 2$) anode materials and their preparation methods. Great perspectives of SiO_2/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, SiO_2/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 ZrO_2 balls in the high energy ball milling procedure was utilized to hydrolyze tetraethyl orthosilicate (TEOS) in the presence of a catalyst (HNO_3 or NH_4OH) and acetylene black. Since this synthesis method yields hardly agglomerated SiO_2/C composite with a particle size of 100 μm orders and a poor distribution of carbon and SiO_2, DBM was introduced into the synthesis pathway to obtain SiO_2/C nanocomposites consisting of highly dispersed carbon nanoparticles on fine amorphous SiO_2 particles. As a result, the SiO_2/C nanocomposite prepared using HNO_3 catalyst, heat treatment at 600 °C in a N_2 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 SiO_2/C agglomerates of ~2 μm in size. Further attempt to decrease the particle size and improve the electrical properties of the SiO_2/C nanocomposite involved some modifications of the synthesis route through the employment of an ammonia catalyst, a polyvynilpyrrolidone (PVP) dispersing agent and heat treatment at 900 °C in a N_2 + 3% H_2 atmosphere. The obtained material exhibited the initial charge capacity of 760 mAh g^{-1} (1121 mAh g-SiO_2^{-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 SiO_2 particles size to a few hundreds of nanometer, which presumably restricts access to full lithium storage capacity of SiO_2 anode. In Chapter 3, nano-SiO_2/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-SiO_2/C composites containing nano-agglomerates with hierarchical fractal morphology and SiO_2 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 mAh g^{-1} over a voltage range from 0.01 to 3.0 V versus Li/Li^+. After annealing at 900 °C in a N_2+3% H_2 atmosphere and high-energy DBM process, the obtained dry-milled nano-SiO_2/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 SiO_2 and carbon inhibited the electrochemical properties of the nano-SiO_2/C composite. In Chapter 4, SiO_2/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 SiO_2/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 SiO_2 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 SiO_2/C nanocomposite prepared with 0.1 mol L^{-1} sucrose concentration exhibited an initial charge capacity of 848 mAh g^{-1} (1344 mAh g SiO_2^{-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.