Synthesis of Silicon-based Nanoparticles by Induction Thermal Plasma for Lithium Ion Battery

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論 文 名　：Synthesis of Silicon-based Nanoparticles by Induction Thermal Plasma for Lithium Ion Battery（誘導結合型熱プラズマによるリチウムイオン電池用のシリコンナノ粒子の合成）

区　　分　：甲

論 文 内 容 の 要 旨

Induction thermal plasma (ITP) attracts great attention due to its excellent properties like extremely high temperature (>10^4 K), high chemical reactivity, rapid quenching effect (10^3~10^6 K/s) and electrodeless discharge. As the development of lithium ion batteries (LIBs), interests in new anode materials with higher energy density increased exponentially. Silicon (Si) is proposed as the most appealing candidate of anode material, because Si can provide a highest charge storage capacity of 4200 mAh/g ($Li_{22}Si_5$), which is approximately 10 times higher than graphite as anode. However, the irreversible volume expansion of up to 400% during charge and discharge for silicon and intrinsic low electrical conductivity frustrate the replacement of graphite anode severely. Some special strategies were applied to overcome those problems, such as silicon nanoparticles (SiNPs), amorphous silicon (a-Si) materials and applying carbon coating on SiNPs. In this dissertation, silicon-based materials with these complicated structure are synthesized with ITP method, and the formation mechanisms are also investigated.

In chapter 1, the method of ITP is reviewed and the objective of this dissertation is presented.

In chapter 2, a-SiNPs are successfully synthesized by induction thermal plasma with additional counter-flow quenching gas, since a-Si shows smaller volume variation compared with crystalline silicon (c-Si). The obtained a-SiNPs show totally different morphology with c-Si, that amorphous phase is characterized with random shapes and smaller diameters (<5 nm), while crystal phase can be identified with spherical shape and much larger size. The amount ratio of a-SiNPs is improved from 33% to 64% with quenching gas flow rate, and the quenching rate increases from 3.2×10^4 to 8.9×10^5 K/s which is demonstrated by numerical studies. The increased quenching rate promotes nucleation and the number of nuclei increases subsequently. Therefore, larger amount of small particles (<5 nm) are synthesized, while amorphous is thermodynamically preferable in such small size for silicon.

In chapter 3, SiNPs with carbon coating are successfully fabricated in one-step by ITP method and ethylene is applied as additional carbon source. The obtained coating is amorphous hydrogenated carbon (a-C:H) with a thickness ranges from 2 to 8 nm. Since the concentration of H radical increases with more ethylene injection, etching effect for sp^2 bonds is enhanced. Then more sp^2 hybrid orbitals will be destroyed and the ratio of sp^2 in final products will be lower. For the same reason, hydrogen content in the carbon coating will be lower with more ethylene injection.

In chapter 4, the effect of hydrocarbon sources (methane, ethylene, and acetylene) on the formation of SiNPs as well as a-C:H coating are investigated. The formation of unfavorable SiC can be identified in all

cases and the amount increases from 2% to 22% with initial C/Si ratios. Graphene flakes are fabricated in the cases of methane and acetylene due to the abundant formation of free C and H atoms. The obtained results of coating characterization reveal that acetylene is a better choice for the preparation of carbon coating at SiNPs in this research due to the highest sp^2 ratio and hardness in comparison with other two carbon sources.

In chapter 5, the effect of sheath gas composition on plasma parameters and the formed silicon-carbon composite are investigated. The ratio of tangential and radial flow rates (T/R), which compose plasma sheath gas, varies from 0.5 to 1. Results shows the plasma shape as well as diameter will be compressed in the case of higher T/R values, which will lead to an enhanced quenching rate on SiNPs while the temperature of methane injection positions will be limited. The improved amount of a-SiNPs and limited H etching effect with higher T/R values further proves this conclusion. For the same reason, formation of unfavorable SiC can be ignored in the case of higher tangential gas flow rate, which can improve the energy density of synthesized particles in batteries.

In chapter 6, the obtained conclusions are marked and some ideas for the future research are presented.

In summary, the obtained results in this research can improve the understanding of formation mechanisms for silicon material in ITP method, which is significant for the design of LIBs with higher energy density and better cycling performance.