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Author(s)	DE JUAN, Lyn Marie Zarsuela
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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 DE JUAN Lyn Marie Zarsuela

学 位 論 文 題 名

One dimensional nano-materials as anode materials for Lithium-ion Battery
(リチウムイオン電池用負極材料としての1次元ナノ材料)

One-dimensional (1D) nanomaterials (NMs), *e.g.*, nanowires (NWs), nanorods (NRs), and nanofibers (NFs), are promising materials with wide range of applications. 1D NMs are known to have high surface area, 1D flow of electrons and ions, ability to restrain mechanical degradation, and have geometrical advantages for in-situ electrochemical probing, which makes them a suitable electronic material, *vis.* energy storage devices. The commonly used method in the production of 1D NMs is by the template-assisted method, however, the removal of the template can damage the produce 1D NMs. Hence, both solution and hydrothermal synthesis of single crystal 1D NMs are widely used methods due to its low cost and feasibility for mass production. This thesis aims to study template-free solution synthesis approaches for growing of 1D NMs: the formation mechanism and their potential application as anode materials for rechargeable Lithium-ion battery (LIB). Materials of interest include β -Sn and spinel oxides, *vis.* ZnV_2O_4 , for their good performance as anode materials for LIB.

This study first focused on new synthesis approach to grow β -Sn NRs. The capping property of the ligand or the difference in the surface energy of the material's crystallographic planes can direct the formation of 1D NMs. The former is the basis for the colloidal synthesis of 1D NMs whereas the latter is an important factor to grow different morphology in materials with anisotropic crystal structure. β -Sn has an anisotropic crystal structure, *i.e.*, tetragonal. However, when β -Sn nanoparticles (NPs) were chemically produced at high temperature, the spherical shape was formed despite using different capping ligands. This can be attributed to the low melting point of bulk β -Sn, *i.e.* 232 °C. Hence, this study proposed to grow 1D β -Sn NMs based on lowering the synthesis temperature in a viscous synthesis solution to manipulate the kinetics of the particle nucleation and growth. The results demonstrated that single crystalline β -Sn NRs growing along [001] direction with tunable aspect ratios were successfully formed at below room temperature. When the synthesis temperature was decreased from 26 °C to 10 °C, the morphology of the produced particle varied from spherical to rod-like with 2.5 aspect ratio. A further decrease in the synthesis temperature to 5, 0, -10, and -15 °C increases the aspect ratio to 4.8, 11.1, 15.8, and 22.9, respectively. On the other hand, varying the viscosity of the solution by varying the amount of PVP (poly(vinyl pyrrolidone)) K90 showed that as the viscosity increases, the aspect ratio of the produced rod-like morphology also increases. Hence, both temperature and viscosity can influence the movement of the particles and thus their kinetic energy. Higher kinetic energy particles/ions can attach easily on any surface planes of the nuclei, while lower kinetic energy particle/ions have a preferred attachment on high surface energy planes. The preferred attachment resulted in rod-like morphology leaving the low surface energy planes, *i.e.*, {200} for β -Sn, on its facets. Besides it was found that PVP can bridge two or more particles together, wherein the higher the molecular weight, MW, of the PVP, the longer the polymeric chain and thus can bridge more particles together to form higher aspect ratio NRs. Therefore, in order to grow high aspect ratio β -Sn NRs, both high MW of ligand that bridges more particles together, and slow particle mobility (lower temperature, more viscous solution), *i.e.*, still enough for lattice realignment, are necessary.

The formed β -Sn NPs with different aspect ratios through the variation of the synthesis temperature was examined under the electrochemical test, *i.e.*, as anode material for LIB. Due to the promising

properties of the rod-like morphology, it was observed that β -Sn NRs exhibited better cycling stability compared to that of the spherical β -Sn NPs. This is due to the strain relaxation effect of the NRs that can buffer large volumetric change. However, a closer examination on the effect of β -Sn NRs with different aspect ratios revealed that lower aspect ratio NRs have better cycling stability, *i.e.*, almost 100% coulombic efficiency, compared to that of higher aspect ratio NRs. It is found that the higher stability of the low aspect ratio NRs relates to the formed LiF-rich solid electrolyte interface, SEI, layer. For β -Sn, (100) and (001) plane can dictate the produced SEI layer, *i.e.*, mainly $LiCO_3$ with electrolyte uptake and LiF with other organic molecules respectively. LiF is known to prevent the further degradation of the electrolyte and improve the ionic conductivity from the solution to the electrode, and hence desirable. Based on our calculation, since β -Sn NRs have (001) tip and (100) side facets, lower aspect ratio NRs have 9 times total surface area of the active (001) surface compared to that of the high aspect ratio NRs, hence should have higher amount of LiF F-containing SEI layer that contributes to the cycle stability. This result agrees well with our XPS result, wherein low aspect ratio NRs have higher LiF F-containing SEI compounds compared to that of the high aspect ratio NRs. This result also agrees well with impedance analysis, wherein, the low aspect ratio NRs have lower SEI resistance and an order of magnitude higher Li^+ diffusion compared to that of the high aspect ratio NRs. These results elucidate the reason for the better performance of low aspect ratio NRs compared to that of the high aspect ratio NRs in addition to the morphology effect in comparison to that of the spherical NPs.

Unlike that of β -Sn, *i.e.*, alloying type anode material, spinel structured materials such as ZnV_2O_4 , is a conversion type anode material. Spinel structure materials are known to be crystallographically porous, *i.e.* with 56 empty tetrahedral sites and 16 empty octahedral sites, and are expected to easily accommodate small guest ions such as Li^+ within its interstitial space. However, the short distances and coulombic interactions between the guest ions and the ions on tetrahedral and octahedral sites prevent the simultaneous occupation, and hence Li^+ can be introduced chemically and electrochemically instead. Zn can form an alloy with Li, while V undergoes redox reaction upon lithiation and delithiation. Conversion anode materials are known to have lower gravimetric capacities compared to that of the alloying materials but with better volumetric capacities and less volumetric change. However, conversion type anode material still experienced large volumetric change that is detrimental as anode material for lithium-ion battery, hence 1D nanostructure is preferable to buffer large volumetric change as that of β -Sn. In this study, 1D ZnV_2O_4 , a spinel compound, was produced by hydrothermal method followed by calcination at 600 °C under 3% H_2/N_2 . Zinc nitrate and ammonium vanadate with 1:2 mole ratio serve as the reactants in the formation of fibrous like ZnV_2O_6 using the hydrothermal synthesis. These fibrous ZnV_2O_6 were reduced to form ZnV_2O_4 and was examined under electrochemical test as anode material for LIB. By varying the calcination condition used in the synthesis, it is found that spherical ZnV_2O_4 NPs and ZnV_2O_4 NWs were synthesized and the NWs were produced for the first time. Both structures showed good cycle stability when being used as anode materials for LIB, though it was observed that the NW structure resulted to a higher capacity at high current density, *i.e.* 5 A/g.

This research deals with the synthesis and application of 1D NMs as anode material for LIB, wherein: (a) new approach in the synthesis and formation of β -Sn NRs were shown and proposed, (b) first study on the combined effect of both the 1D morphology and the formed SEI layer, *i.e.* the LiF-rich F-containing SEI layer induced by the (001) tip of the rod, of β -Sn NRs as anode material for LIB was presented, and (c) first synthesis and application of 1D ZnV_2O_4 as anode material for LIB were observed.