Sn-Ge-Se nano-structured composite materials as a high capacity anode material for Li-secondary batteries

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High capacity anode materials are highly required for Li-secondary batteries especially in mobile and electric vehicle applications. However, commercialized anode materials based on graphite allow limited gravimetric capacity (372 mAh/g) and hamper its wider application to high energy density battery system. Although Sn has high theoretical capacity (992 mAh/g) and is regarded as a strong candidate to replace graphite based materials, it shows high volume expansion during Li⁺ insertion and extraction reaction. Among various efforts to reduce such cyclic degradation of Sn-based materials, tin-based amorphous oxide (TCO) showed highly enhanced cyclic performance with 90% of initial capacity after 100 cycles [1]. Homogenous amorphous phase surrounding active Sn-O core effectively suppressed the stress induced by the large volume change during intercalation reactions. However, formation of Li₂O cannot be avoided due to oxygen content which causes serious capacity loss. Tin based chalcogenide composite (TCC) materials, thus has been proposed to provide amorphous matrix as well as non-oxide environments [2]. Lee et al. successfully formed nano-sized structure of SnS and Ge-S based amorphous phase but also suffered from irreversible reaction of Li₂S formation. In this study, we designed and synthesized Se based chalcogenide composite materials using Se in order to minimize the capacity loss due to irreversible reactions improving coulombic efficiency.

Sn-Ge-Se compositions were selected on the boundary of glass formation range and synthesized by melt-quenching method using silica ampoule and locking furnace at 1000 °C for 12 hrs. The obtained composite materials were grinded into powders with ball mill and SPEX mills under 100 µm in size. The powders were thermally analyzed by DSC and their phases were examined with X-ray diffraction. SEM and TEM also inspected the micro- and nano-structure of the composites. Electro-chemical analysis were performed to evaluate the anodic performance of the composites after fabrication of CR 2016 coin type half cells.

DSC result showed endothermic reaction of αSnSe → βSnSe + L₂ which proved the formation of SnSe. SnSe phase has been further confirmed by the x-ray diffraction of the composites. Broad X-ray peaks implied the nano-sized crystalline phases within the composite materials.

SEM analysis showed the grinded powders are well distributed showing no characteristic morphologies such as SnS sheet structure. EDS analysis supported the composition of the composites were well preserved without serious contamination oxygen. High resolution TEM of the composites (Fig. 1) clearly showed the well dispersed nano-crystalline phases within amorphous phases. The crystalline phase was identified as SnSe coinciding to the results obtained by DSC and XRD.

Electrochemical analysis showed high cyclic stability compared to previously reported S-based Sn composites. Coulombic efficiency was also highly improved as shown in Fig. 2. Irreversible reaction due to Li₂Se formation was observed at the first discharge reaction. SnSe nano-crystals was believed to be the active alloying elements while Ge-Sn-Se amorphous phases effectively relieved the stress induced during the alloying/de-alloying reactions. Well distributed nano-structure seems to be responsible for the high cyclic stability as well as improved Coulombic efficiency.

References

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