

## Mechanically Lithiated $\text{CeSn}_x$ as Anode for Rechargeable Lithium Battery

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Recently, in the search for anode materials for use in rechargeable lithium batteries, there has been considerable interest in tin based intermetallic compounds because of their large latent capacities in comparison with carbon materials (1-8). In the present study, we focused on mechanically lithiated Ce-Sn alloys to improve irreversible capacity at the first cycle and cyclability, and synthesized  $\text{Li}_x\text{CeSn}_y$  ( $\text{Li}_{3.8}\text{CeSn}_3$  and  $\text{Li}_2\text{CeSn}_2$ ) using mechanical alloying (MA). The electrochemical performance of electrodes consisting of the compounds was investigated, and X-ray and neutron diffraction experiments were carried out to clarify the electrode reaction mechanism.

### EXPERIMENTAL

Mechanically lithiated Ce-Sn alloys, such as  $\text{Li}_{3.8}\text{CeSn}_3$  and  $\text{Li}_2\text{CeSn}_2$ , were prepared by mechanical alloying. The detailed procedure was described in elsewhere. X-ray diffraction was done on the MA samples before and after charging to identify phases. Electrochemical performance of the electrodes was estimated with a three-electrode cell. The working electrode consisted of the  $\text{Li}_{3.8}\text{CeSn}_3$  (or  $\text{Li}_2\text{CeSn}_2$ ) powder and copper mesh. No conductive materials and binders were used for the construction of the electrodes. In the test cell, both counter and reference electrodes were lithium metal sheets. 1 M  $\text{LiClO}_4$  dissolved in propylene carbonate was used as an electrolyte. The cell performance was evaluated galvanostatically at a current density of  $0.4 \text{ mA cm}^{-2}$  for both charge and discharge and a potential range of 0.0-2.0 V at 303 K.

### RESULTS AND DISCUSSION

The discharge (Li extraction) curves of the mechanically lithiated Ce-Sn alloy ( $\text{Li}_x\text{CeSn}_y$ ) electrodes were almost the same profile as those of the  $\text{CeSn}_3$  electrode and their potential plateaus were obviously lower than those of elemental tin electrode, suggesting that the active material in the  $\text{Li}_x\text{CeSn}_y$  electrodes is predominantly  $\text{CeSn}_3$ .

As shown in Fig. 1, the  $\text{CeSn}_3$  electrode exhibited poor cyclability, whereas the drastic improvement of cyclability was observed in the  $\text{Li}_x\text{CeSn}_y$  electrodes. The  $\text{Li}_x\text{CeSn}_y$  electrodes showed excellent performance not only on the cyclability, but also on reversibility at the first cycle.

From XRD analysis, a main phase in both  $\text{Li}_{3.8}\text{CeSn}_3$  and  $\text{Li}_2\text{CeSn}_2$  belonged to  $\text{Li}_2\text{Ce}_2\text{Sn}_3$ , and the profiles of XRD patterns did not vary after charge-discharge cycling. This appears to indicate that  $\text{Li}_2\text{Ce}_2\text{Sn}_3$  plays a role as an electrochemically non-active matrix phase. The reason why no  $\text{CeSn}_3$  phase was observed in the XRD patterns would be that the  $\text{CeSn}_3$  phase was finely dispersed in the  $\text{Li}_2\text{Ce}_2\text{Sn}_3$  matrix phase. The neutron scattering experiment was carried out to confirm the existence of  $\text{CeSn}_3$  phase in  $\text{Li}_x\text{CeSn}_y$ . Figure 2 illustrates the radial distribution function (RDF) of  $\text{Li}_x\text{CeSn}_y$ . The interatomic correlation (333 pm) which belongs to Ce-Sn and Sn-Sn in  $\text{CeSn}_3$  phase was clearly observed in the RDF patterns of both  $\text{Li}_{3.8}\text{CeSn}_3$  and

$\text{Li}_2\text{CeSn}_2$ . This result is considered to support the existence of  $\text{CeSn}_3$  phase.

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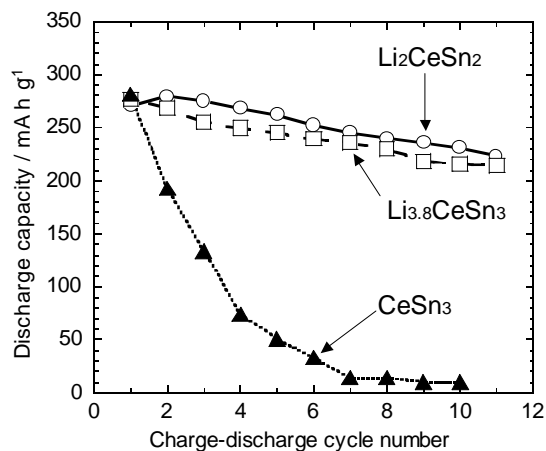


Figure 1 Cycle life performance of the  $\text{CeSn}_3$ ,  $\text{Li}_{3.8}\text{CeSn}_3$ , and  $\text{Li}_2\text{CeSn}_2$  electrodes.

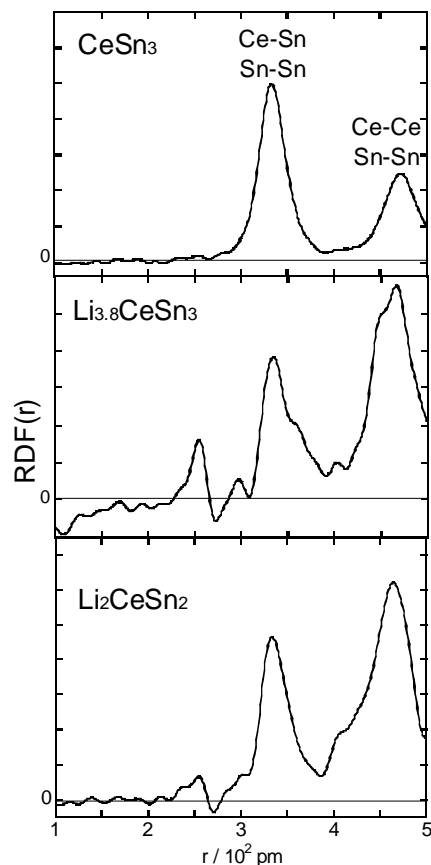


Figure 2 The radial distribution functions (RDF) of  $\text{CeSn}_3$ ,  $\text{Li}_{3.8}\text{CeSn}_3$ , and  $\text{Li}_2\text{CeSn}_2$ .