

Electrochemical Reactivity of Magnesium Ions With Sn-Based Binary Alloys

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Magnesium ion rechargeable battery systems receive considerable interest as candidate post-lithium systems. However, the exceedingly slow solid-state diffusion of the divalent Mg^{2+} cations has been a bottleneck in electrochemical insertion/extraction [1]. To date, there have been only a few kinds of anode materials such as Bi, Sb, Sn and Bi-Sb alloys [2,3]. Other potential anode materials such as alloy anodes, should be investigated as has been extensive in the case of lithium. In this paper we explored tin (Sn) alloys (Cu-Sn, In-Sn, Pb-Sn) as possible candidates for negative electrode materials.

All electrochemical experiments were performed in an Ar-filled glovebox (H_2O , $\text{O}_2 < 1\text{ppm}$). A three-electrode electrochemical cell was employed using Mg rods as the counter and reference electrodes. Sn, $\text{Pb}_{0.4}\text{Sn}_{0.6}$, $\text{In}_{0.5}\text{Sn}_{0.5}$, Cu_6Sn_5 and Cu_3Sn were used as the working electrodes after cleaning with acetone and/or ethanol. A 0.95 mol dm^{-3} solution of EtMgBr in THF (ca. 200ppm H_2O) was used as the electrolyte.

Figure 1a displays cyclic voltammograms (CV) for pure Sn, where combination of reduction and oxidation waves were clearly observed. The redox peaks were observed at +0.14 V and +0.25 V vs. Mg, respectively, comparable with the potential of charge-discharge plateaus, where $\text{Sn} + 2\text{Mg}^{2+} + 4\text{e} = \text{Mg}_2\text{Sn}$ is suggested [3]. The maximal current density was as large as about $12\text{ }\mu\text{A cm}^{-2}$.

Insertion/desertion of Mg ions were also successful in In-Sn and Pb-Sn alloys. Fig. 1b shows the CV for $\text{In}_{0.5}\text{Sn}_{0.5}$ alloy which consist of In_3Sn and $\text{In}_{0.2}\text{Sn}_{0.8}$, showed broad redox peaks, possibly indicating that both In_3Sn and $\text{In}_{0.2}\text{Sn}_{0.8}$ phases are active against Mg. Shown in Fig. 1c is the case of eutectic Pb-Sn alloy, several reduction peaks were seen (0.04 V, 0.08 V, and 0.13 V vs. Mg), while one oxidation peak was seen (+0.29 V vs. Mg at 10th cycle). Since Pb-Sn system is a typical eutectic alloy where Pb-rich and Sn-rich phases coexist, the several cathodic peaks imply that both Sn-rich and Pb-rich phases can react electrochemically to form such as Mg_2Sn and Mg_2Pb . The rather asymmetric CV curve may imply that, while Pb-rich and Sn-rich phase react with Mg individually, the Mg dissolution undergo in a cooperative way to reform Pb-Sn alloy: it is possible that the reformation of Pb-Sn alloy is a driving force for the demagnesiumation process.

Figure 2 displays the CV for Sn, In-Sn and Pb-Sn at 10th cycle. The redox peaks of In-Sn and Pb-Sn alloys reached as large as about $130\text{ }\mu\text{A cm}^{-2}$, ten times larger than that of elemental Sn. Here, taking into account that the melting points of In-Sn and Pb-Sn alloys (about 120 °C and 180 °C, respectively) are much lower than that of elemental Sn (232 °C), alloys with lower melting points can be advantageous in terms of Mg diffusion rate.

[1] E. Levi, M. D. Levi, O. Chasid, and D. Aurbach, *J. Electroceram.* **22**, 13 (2009).

[2] T. S. Arthur, N. Singh, and M. Matsui, *Electrochem. Commun.* **16**, 103 (2012).

[3] N. Singh, T. S. Arthur, C. Ling, M. Matsui, and F. Mizuno, *Chem. Commun.*, **49**, 149 (2013).

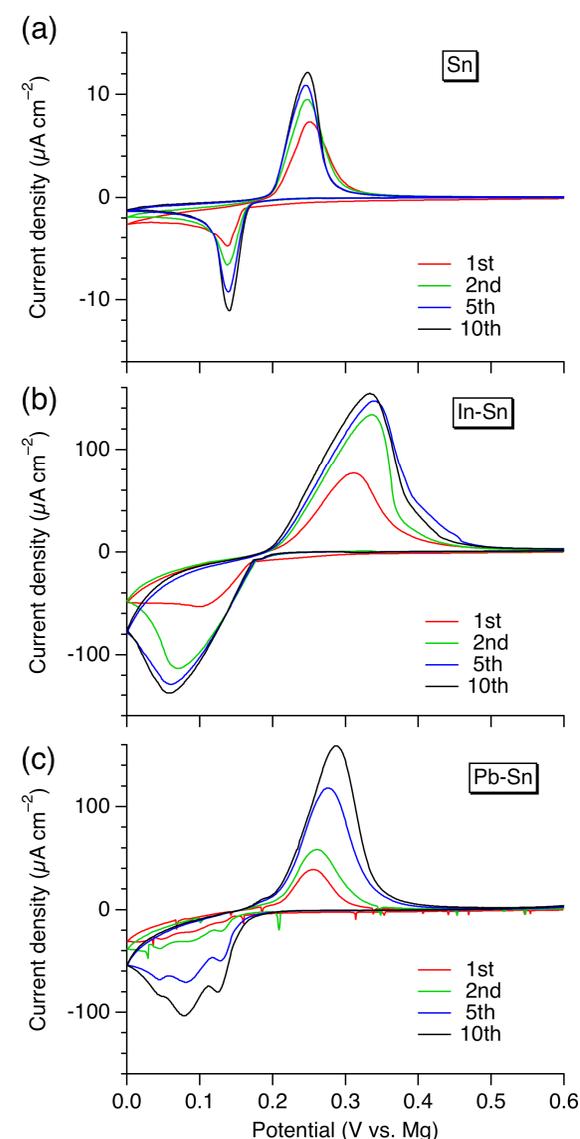


Figure 1. CV data for (a) Sn, (b) Pb-Sn, and (c) In-Sn electrodes cycled between +0.05 V vs. Mg and the open circuit potential.

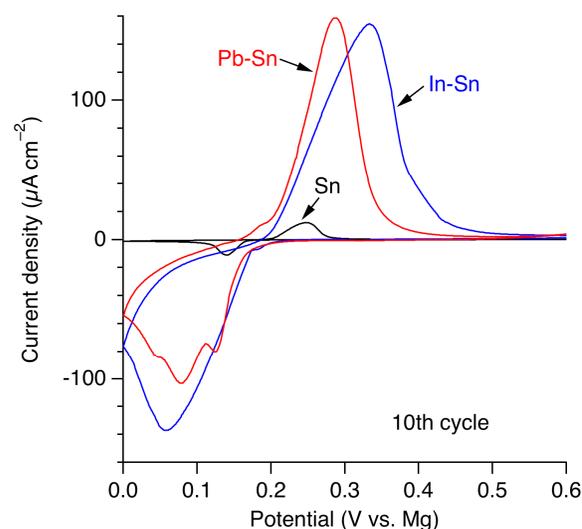


Figure 2. CV data of the 10th cycle for the Sn, In-Sn, and Pb-Sn electrodes.