

Co-Doped $Co_x Cu_{6-x} Sn_5$ Alloys as Negative Electrode Materials for Rechargeable Lithium Batteries

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A series of Co-doped $\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5$ ($0 \le x \le 2$) alloys were prepared by mechanical alloying, followed by annealing at 400°C. The Co-doped alloys show the same structure as the $\text{Cu}_6 \text{Sn}_5$, which can be indexed to a hexagonal NiAs-type cell, but differ in the electrochemical performance as the anodes of Li-ion batteries. The results of ex situ X-ray diffraction analysis indicate the different Li alloying mechanism among $\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5$. The metastable intermediate phases of $\text{Li}_2 \text{Co}_y \text{Cu}_{1-y} \text{Sn}$ formed during the Li-ion insertion process of $\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5$ become unstable and even undetectable with increasing amounts of Co substituted. A proper amount of Co-doped alloy, $\text{CoCu}_5 \text{Sn}_5$, showed improved cycling stability at the expense of capacity, whereas a heavy Co-doped alloy, $\text{Co}_2 \text{Cu}_4 \text{Sn}_5$, resulted in poor cycling ability. The crystal and electronic structure, thermodynamic stability of $\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5$ and half-lithiated alloy, $\text{Li}_2 \text{Co}_y \text{Cu}_{1-y} \text{Sn}$, as well as the average voltage of alloying reaction in terms of different discharge depths were investigated using first-principles density-functional theory with pseudopotentials and plane wave basis. © 2006 The Electrochemical Society. [DOI: 10.1149/1.2374949] All rights reserved.

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Lithium-ion batteries based on a carbon/graphite anode and a transition metal-oxide cathode have been commercially used in popular portable devices such as cellular phones and laptop computers for about 15 years. One of the most interesting and challenging goals is to develop increased capacity electrode materials in order to increase the battery energy density. The conventional anode material, graphite, has a theoretical maximum capacity of 372 mAh/g, or a volumetric capacity of 818 Ah/L (the density of graphite is 2.2 g/cm^3). Metals and alloys present an attractive alternative to graphite as anode materials for lithium-ion batteries due to the high capacity, an acceptable rate capability, and operating potentials well above the potential of metallic lithium. In particular, the intermetallic compounds (M'M) show the most promising possibilities.¹⁻³ It typically consists of an "inactive phase M'," which does not react with lithium, and an "active phase M," which reacts with lithium. Introducing an inactive phase M' can reduce the volume expansion/ contraction to some extent, thus improving its cycling performance. According to the lithium-ion alloying mechanism, the alloys can be divided into two groups. The first one refers to those alloys in which the reaction of lithium results first in the formation of Li_xM'M as an intermediate phase, while further reaction leads to a mixed phase of the disordered Li_vM alloy and metal M', and the initial intermetallic alloys are reformed when lithium is extracted from the alloys during charge, such as Cu_6Sn_5 ,^{1,4} InSb,^{5,6} etc. The other group refers to those alloys in which the reaction of lithium in the M'M results directly in the formation of a disordered LixM alloy and metal M' matrix, but M' cannot recombine with M to reform the initial intermetallic compounds during the charge, such as Sn-Mn,² Sn-Fe,³ and Co-Sn,' etc. Therefore, studies of the intermetallic alloys containing both the group I and II inactive phases M' and active phase M would appear to be of great interest. In the present work, we choose the inactive phase Co of group II to substitute the inactive phases Cu of group I in Cu₆Sn₅ alloy and study its electrochemical properties.

To date, Cu_6Sn_5 has been widely studied, including the Li-ion alloying mechanism,^{4,8} the preparation of nanosize crystalline and amorphous materials,^{9,10} somewhat regular-shaped materials using different techniques,¹¹ using thin film electrodes¹² and so forth, to improve its cycling stability. In the present work, we systematically studied the effects of partial substitution of Co for Cu on the electrochemical properties of the $Co_xCu_{6-x}Sn_5$ electrodes by means of charge/discharge test and ex situ X-ray diffraction (XRD) analysis. The crystal and electronic structure, the formation energy and there-

fore the thermodynamic stability, and the change in the bonding character on lithiation provide important information that can be extracted from the first-principles calculations. Such analysis regarding battery materials has been done in the past using the total¹³ or difference^{14,15} charge density and electronic density of states. In the present work, we also apply the first-principles calculations method to investigate the crystal and electronic structure, the thermodynamic stability of $Co_xCu_{6-x}Sn_5$ and lithiated alloy, and Li₂Co_yCu_{1-y}Sn, as well as the average lithium insertion voltage.

Methodology

Experimental.— A series of Co-doped $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$ ($0 \le x \le 2$) alloys, i.e., Cu_6Sn_5 , $\text{Co}_{0.5}\text{Cu}_{5.5}\text{Sn}_5$, CoCu_5Sn_5 , and $\text{Co}_2\text{Cu}_4\text{Sn}_5$, were synthesized by mechanical ballmilling a stoichiometric amount of metallic powder Cu, Co, and Sn for 12 h under Ar atmosphere using a high-energy planetary monomill pulverisette 6 (Fritsch GmbH. Inc., Germany). After milling, the powders were pressed into pellets and heat-treated at 400°C for 12 h under Ar flow in order to obtain single-phase, well-crystalline intermetallic compounds. The gray brittle products were then ground and sifted to approximately 400 mesh.

XRD patterns of the powdered samples were obtained using an X-ray diffractometer (Bruker Advance8) with Cu K α radiation. The diffraction data were collected at 0.015 step widths over a 2 θ range from 25 to 80°. The structural parameters were refined by Rietveld analysis using the computer program RIETAN 2000. The structural model used is the NiAs-type structure¹⁶ (space group *P6*₃*mmc*, no. 194) with Sn in 2a sites and Cu in 2c sites.

The electrodes were prepared by mixing 80% alloy powders, 10% carbon black, and $\bar{1}0\bar{\%}$ polyvinylidene fluoride (PVDF) dissolved in *N*-methylpyrrolidinone (NMP). The slurries of the mixture were coated on Cu foil. After coating, the electrodes were dried at 80°C for 10 min to remove the solvent before pressing. The electrodes were cut into sheets 1 cm² in area, vacuum-dried at 100°C for 24 h, and weighed. The typical weight load of active material is about 5 mg/cm². The battery performance of alloy was characterized in a CR2032-type coin cell. Metallic lithium was used as the negative electrode. The electrolyte solution was 1 M LiPF₆/ethlylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 by volume). The cells were cycled at a constant current density of 0.25 mA/cm^2 between 0.0 and2.0 V. Lithium insertion into an alloy electrode was referred to as discharge and extraction as charge. The cell capacity was determined by only the alloy active material.

The crystal structure changes of alloys during charge/discharge were also investigated by ex situ X-ray diffractions monochromated by a graphite crystal. For ex situ XRD experiments, CR2032-type

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Figure 1. Powder XRD patterns of $Co_xCu_{6-x}Sn_5$ alloys: (a) Cu_6Sn_5 , (b) $Co_{0.5}Cu_{5.5}Sn_5$, (c) $CoCu_5Sn_5$, and (d) $Co_2Cu_4Sn_5$. The Miller index for each peak is marked in the figure and the peaks of (002) and (004) are labeled for their shift to the small angle.

coin Li/alloy cells were first charged/discharged to different charge/ discharge states at a current density of 0.05 mA/cm² (ca. 10 mA/g), then the cells were opened in a glove box and the electrodes were washed in DMC solvent. The alloy electrode was immediately transformed to assemble in an ex situ XRD cell in which a polyethylene film was used as a window. Data were collected over the range $20^{\circ} \le 2\theta \le 60^{\circ}$.

Computational.— We have first calculated the total energies of (*i*) unlithiated hexagonal Co-doped Cu–Sn alloys, presented by $Co_xCu_{6-x}Sn_5$ (x = 0, 1, 2, 3, 4, 5, and 6), *ii* partially lithiated states, the cubic structure of Li₂Co_yCu_{1-y}Sn (y = 0, 0.25, 0.5, and 0.75), and *iii* fully lithiated states, the cubic Li_{4.4}Sn. The structure change during lithium insertion or extraction might be very complicated in the real system; we herein deal with only the above three charge/discharge states. Moreover, we also calculated the average voltage for lithium insertion in the alloys. The average voltage for the lithiation reaction from $Co_yCu_{1.2-y}Sn$ to $Li_2Co_yCu_{1-y}Sn$ ($0 \le Li \le 2$) was represented by V_1 , the reaction from $Li_2Co_yCu_{1-y}Sn$ to $Li_{4.4}Sn$ ($2 \le Li \le 4.4$) by V_2 , and the total average voltage during Li insertion from $Co_yCu_{1.2-y}Sn$ to $Li_{4.4}Sn$ by V_3 . The V_1 , V_2 , and V_3 are defined as follows

$$V_{1} = -\frac{(E_{\text{Li}_{2}\text{Co}_{y}\text{Cu}_{1-y}\text{Sn}} + 0.2E_{\text{Cu}}) - (E_{\text{Co}_{y}\text{Cu}_{1.2-y}\text{Sn}} + 2E_{\text{Li}})}{2F}$$

$$(0 \le \mathrm{Li} < 2)$$
[1]

$$V_{2} = -\frac{[E_{\text{Li}_{4,4}\text{Sn}} + (1 - y)E_{\text{Cu}} + yE_{\text{Co}}] - (E_{\text{Li}_{2}\text{Co}_{y}\text{Cu}_{1-y}\text{Sn}} + 2.4E_{\text{Li}})}{2.4F}$$

$$(2 \le \text{Li} \le 4.4)$$
[2]

$$V_{3} = -\frac{[E_{\text{Li}_{4,4}\text{Sn}} + (1.2 - y)E_{\text{Cu}} + yE_{\text{Co}}] - (E_{\text{Co}_{y}\text{Cu}_{1.2-y}\text{Sn}} + 4.4E_{\text{Li}})}{4.4F}$$
$$(0 \le \text{Li} \le 4.4)$$
[3]

where V is the average voltage and E_c is the total energy of compound C or energy per atom for metallic C. The calculation of the average voltage is based on the assumption that Cu is extracted from the alloy hosts instead of Co before the discharge depth of $0 \le \text{Li} \le 2$. This assumption is explained below.

The Cu₆Sn₅ compound and the Co-doped compounds used in the computational study were chosen as a defect Ni₂In structure with Sn occupying 2c position and Cu at the 2a and 2d positions of space group $P6_3/mmc$.¹⁷ The Cu occupancy of the 2d position was 20%; they occupy every fifth trigonal bipyramidal site in the strings of Sn atoms. Li₂CuSn exists in cubic structure of space group Fm3m (no. 225) with Sn atoms at 4a sites, Li at 4b and 8c sites and Cu at 8c sites. The structure information of Li_{4.4}Sn comes from the literature.¹⁸

In order to investigate the relation between the cycle performance improvement and the electronic structure of alloys, we also carried out a series of calculations of the electronic density of states for $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$ (y = 0, 0.25, and 0.75) and the charge-density change in Li_2CuSn and $\text{Li}_2\text{Co}_{0.5}\text{Cu}_{0.5}\text{Sn}$ during lithium alloying. The total energies of all the structures were calculated using Vienna ab initio simulation package (VASP) based on the ultrasoft pseudopotentials formalism¹⁹ within the general gradient approximation (GGA) for conducting the exchange-correlation corrections.²⁰ The valence electrons are expanded in a plane-wave basis set. All considered structures were fully relaxed with respect to changes in volume, shape, and ion positions within a certain unit cell during the self-consistent energy minimization.

The number of atoms per unit cells was 22 for $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5(x = 0, 1, 2, 3, 4, 5, \text{ and } 6)$ and 16 for $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}(x = 0, 0.25, 0.5, \text{ and } 0.75)$, depending on which of the desired sets of *k*-points in reciprocal space were chosen. In all of the calculations, the convergence of the total energy with respect to *k*-point sampling and planewave energy cutoff has been carefully examined. The final set of energies was computed with an energy cutoff of 500 eV for all compounds. The *k*-point number of 62 and 20 for $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5(x = 0, 1, 2, 3, 4, 5, \text{ and } 6)$ and $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}(x = 0, 0.25, 0.5, \text{ and } 0.75)$ has been used, respectively, for the irreducible Brillouin zone integration. The supercell of $\text{Li}_{4,4}\text{Sn}$ was very large with 432 atoms, so a *k*-point grid of $4 \times 4 \times 4$ (4 *k*-points) were used to compute its total energy. When calculating the electronic density of states, 84 *k* points have been used.

Results and Discussion

Characterization of $Co_x Cu_{6-x}Sn_5$.— The typical XRD patterns of $Co_x Cu_{6-x}Sn_5$ alloys are shown in Fig. 1. All compounds show very similar XRD patterns, and all peaks can be ascribed to the signature peaks corresponding to the Cu₆Sn₅ phase. No other phases were observed. It is obvious that the (002) and (004) peaks slightly shift to a small angle, while the other peaks shift to a large angle with increasing amounts of doped-Co content. In order to investigate the change of lattice parameters, we performed the Rietveld refine-

Table I. Rietveld refinement result for $Co_x Cu_{6-x}Sn_5$. *a*, *c*, and *V* are the two lattice constants and cell volume of the structures, respectively. R_{wp} and R_p are the two quantities describing the goodness of fit and the agreement between the calculated and observed intensities, respectively.

		Calculated	Rietveld refinement results				
Samples	Space group	density (g/m ³)	a(=b) (Å)	<i>c</i> (Å)	V (Å ³)	$egin{array}{c} R_{ m wp} \ (\%) \end{array}$	$egin{array}{c} R_p \ (\%) \end{array}$
Cu ₆ Sn ₅	P6 ₃ mmc	8.35	4.196	5.088	77.58	7.12	5.46
Co _{0.5} Cu _{5.5} Sn ₅	P6 ₃ mmc	8.37	4.183	5.095	77.20	8.98	6.23
CoCu ₅ Sn ₅	P6 ₃ mmc	8.36	4.175	5.108	77.10	6.06	4.61
$Co_2Co_4Sn_5$	P6 ₃ mmc	8.44	4.138	5.127	76.03	6.85	5.21



Figure 2. Typical first three charge/discharge curves of Li/alloy cells containing (A) Cu_6Sn_5 , (B) $Co_{0.5}Cu_{5.5}Sn_5$, (C) $CoCu_5Sn_5$, and (D) $Co_2Cu_4Sn_5$. The 10th charge curve of $Co_2Cu_4Sn_5$ is also shown.

ment. The refined lattice parameters are listed in Table I. All patterns were fitted successfully to a hexagonal structure. The refinement results show that the lattice parameter a and the cell volume decrease, while the lattice parameter c increases with the increase in doped-Co content. The calculated densities of all alloys are almost the same.

Electrochemical performance.— Figure 2 shows the typical charge/discharge profiles of $C_{0x}Cu_{6-x}Sn_5$ alloy electrodes. It is clear from Fig. 2 that Cu_6Sn_5 reveals two plateaus on discharge, one at about 0.4 V and the other below 0.15 V vs Li/Li⁺. Accordingly, two regions are observed on the charge, one below 0.5 V and the other between 0.5 and 0.8 V vs Li/Li⁺. The result is in good agreement with the previous reports.^{1,4} The main differences in the charge/discharge profiles of the four alloys lie in the shape of discharge plateau at about 0.4 V and the charge plateau around 0.8 V. Cu_6Sn_5 shows more obvious flat plateaus, but the plateaus become gradually undistinguishable with increasing amounts of Co content and finally become invisible for $Co_2Cu_4Sn_5$. Table II summarizes the first charge/discharge capacity and coulomb efficiency of $Co_xCu_{6-x}Sn_5$ alloy electrodes. While the Cu_6Sn_5 and $Co_2Cu_4Sn_5$ show the larger reversible capacity and better first charge/discharge efficiency, the reason is not clear.

According to the previous reports, ^{1,4,8} the two plateaus of Cu₆Sn₅ at discharge process are attributed to distinct single first-order transitions, namely, Cu₆Sn₅ \rightleftharpoons Li₂CuSn (above 0.15 V) and Li₂CuSn \rightleftharpoons Li_{4,4}Sn + Cu, respectively. The reverse reactions occur during charge, but both the Li_{4,4}Sn and the Li₂CuSn can exhibit a range of Li stoichiometries. The 0.4 V discharge plateau is associated with the coexistence of Cu₆Sn₅ and Li₂CuSn phase, and the 0.8 V charge plateau can be indexed to the coexistence of Li_{2-x}CuSn and Cu₆Sn₅ phases. In view of the charge/discharge shape, it seems that the metastable phase of Li₂CuSn becomes

Table II. Summaries in the first charge/discharge capacity and efficiency of the alloys.

Alloy	1st discharge capacity (mAh/g)	1st charge capacity (mAh/g)	Coulomb efficiency (%)
Cu ₆ Sn ₅	620	481	77.6
Cu _{0.5} Cu _{5.5} Sn ₅	577	418	72.4
Co1Cu5Sn5	581	420	72.4
$\mathrm{Co}_2\mathrm{Cu}_4\mathrm{Sn}_5$	711	532	74.7



Figure 3. Capacity vs cycle number of Li/alloy cells containing $Co_{x}Cu_{6-x}Sn_{5}$ at a current of 0.25 mA/cm² between 0 and 2.0 V; (a) $Cu_{6}Sn_{5}$, (b) $Co_{0.5}Cu_{5.5}Sn_{5}$, (c) $CoCu_{5}Sn_{5}$, and (d) $Co_{2}Cu_{4}Sn_{5}$.

gradually unstable to sustain the plateau of 0.4 V during the discharge and that of 0.8 V during the charge. As a result, both plateaus disappear for Co₂Cu₄Sn₅, as shown in the curve of Fig. 2d. The charge/discharge profile of Co2Cu4Sn5 looks like those of FeSn2 and $CoSn_2^7$ which have a quite different Li-alloying mechanism from that of Cu₆Sn₅; the reaction of lithium in these alloys results in the formation of a disordered Li_xSn alloy surrounded by a Fe or Co matrix during the first discharge, and Fe or Co could not recombine with Sn to reform the initial intermetallic compounds during the charge. However, in the subsequent charge/discharge profiles, even after ten cycles, the distinguished three plateaus, a signature of Liion insertion reaction in pure Sn alloy, were not observed, which is different from the case of Li alloying in FeSn₂ and CoSn₂. We suspect that the Co-doped half-lithiated states, Li₂Co_vCu_{1-v}Sn, form during the charge/discharge of Co_xCu_{6-x}Sn₅ and play an important role on the curve shape changes of the alloys.

Figure 3 compares the charge-discharge cycling of Li/alloy cells containing $Co_x Cu_{6-x} Sn_5$ (x = 0, 0.5, 1, and 2) alloys at a current rate of 0.25 mA/cm² between 0 and 2.0 V. The capacity vs cycle number declines rapidly for Cu₆Sn₅ and the heavy Co-doped Co₂Cu₄Sn₅ alloy (curves a and d in Fig. 3), while the small amount of Co-doped Cu-Sn alloys, i.e., Co_{0.5}Cu_{5.5}Sn₅ and CoCu₅Sn₅, show improved cycling stability, as shown in curves b and c in Fig. 3. It can also be observed that the CoCu₅Sn₅ has the best cycling performance with a significant amount of reversible capacity of 300 mAh/g over 50 cycles. As pointed out above, Co-doped alloy proceeds probably in homogeneous lithium alloying reaction (S-shaped charge/ discharge curve), especially for the Co₂Cu₄Sn₅, while Cu₆Sn₅ proceeds in a coexistence of two phases. However, the phase change does not explain why the proper amount of Co-doped alloys show improved cycling performance. This is different from the case of lithium intercalation in the metal oxide electrode materials (typically used for the positive electrode materials) in which a homogeneous intercalation normally behaves as a stable cycling profile compared with the two-phase reaction, while for the lithiation reactions in most alloys it has been demonstrated that the structural integrity is not likely to be maintained because a large volume change occurs.

Lithium alloying mechanism.— In order to shed some light on the issue of whether or not the Co-doped alloys show a similar Li alloying mechanism with that of Cu_6Sn_5 , ex situ XRD measurements were carried out on Cu_6Sn_5 , $CoCu_5Sn_5$, and $Co_2Cu_4Sn_5$ during the charge and discharge process. Figure 4 shows the XRD patterns of as-prepared alloy powders (curve a) and the ex situ XRD of their electrodes at appropriate charged (unlithiated) or discharged (lithiated) depth. Figure 4 reveals clearly that the alloying mechanism of the alloys changes with the increasing amount of Co content.



Figure 4. Ex situ XRD patterns of (A) Cu_6Sn_5 , (B) $CoCu_5Sn_5$, and (C) $Co_2Cu_4Sn_5$ at different charge/discharge states. For Cu_6Sn_5 , (a) the asprepared alloy powders, (b) the state of discharged to 200 mAh/g at 0.4 V, (c) discharged to 0.0 V, (d) recharged to 400 mAh/g at 0.75 V, and (e) 1.5 V were tested. For the Co-doped alloys, (a) the as-prepared alloy powders, (b) the state of discharged to 180 mAh/g (0.15 V for $CoCu_5Sn_5$ and 0.12 V for $Co_2Cu_4Sn_5$), (c) the state of discharged to 230 mAh/g (0.12 V for $CoCu_5Sn_5$ and 0.10 V for $Co_2Cu_4Sn_5$), (d) discharged to 0.0 V, (e) recharged to 0.65 V (300 mAh/g for $Co_2Cu_4Sn_5$), and (f) 1.5 V were tested.

First, for the Cu₆Sn₅ electrode, when the cell was discharged to 200 mAh/g, around 0.4 V vs Li/Li⁺, the appearance of diffraction peaks located at 24.5 and 40.5° confirm the formation of Li₂CuSn phase as shown in the b curve of Fig. 4A. The Li_xSn ($0 \le x \le 4.4$) phase identified by the broad peaks of 23.0 and 38.5° was observed when the cell reaches 0.0 V vs Li/Li⁺ (curve c of Fig. 4A). When the cell was recharged to 400 mAh/g (at the voltage of 0.75 V for Cu₆Sn₅), the peaks of Li_xSn vanish and the peaks of Li₂CuSn and Cu₆Sn₅ appear (curve d in Fig. 4A), and the Li₂CuSn phase completely transforms to Cu₆Sn₅ when charged to 1.5 V vs Li/Li⁺ (curve e in Fig. 4A). The results are in good agreement with that reported by in situ XRD analysis.^{4,8}

Second, in the case of $CoCu_5Sn_5$, the ex situ XRD patterns show similar changes to that of Cu_6Sn_5 during charge/discharge. However, the first difference is that the diffractions of the half-lithiated alloy, $Li_2Co_yCu_{1-y}Sn$ as mentioned above, are weaker than those of Li_2CuSn formed during the lithiation of Cu_6Sn_5 (see curves b and c of Fig. 4B). Another, more important difference appears when the cell was discharged to 230 mAh/g at 0.12 V for $CoCu_5Sn_5$. The ex situ XRD data shows that there are three phases coexisting in the product, the original $CoCu_5Sn_5$ identified by the diffraction peak of 30° , the $Li_2Co_yCu_{1-y}Sn$ identified by the peaks around 24.5 and 40.5° , and the Li_xSn phase (around 23 and 38.5°) as shown in curve



Figure 5. Enlarged XRD patterns of Fig. 4 around 30.0°

c of Fig. 4B. This three-phase coexistence phenomenon cannot be found in our ex situ XRD experiment of Cu_6Sn_5 and the in situ XRD experiment reported previously.^{4,8} The peaks of $Li_2Co_vCu_{1-v}Sn$ disappear and the peaks of Li_xSn become strong when the cell reaches 0.0 V (curve d of Fig. 4B). This three-phase coexistence phenomenon can also be observed when the cell was charged to 300 mAh/g at 0.65 V for CoCu₅Sn₅ (curve e in Fig. 4B), and then the phases transform to CoCu₅Sn₅ when charged to 1.5 V vs Li/Li⁺ (curve f in Fig. 4B). In order to identify whether the recharged product is a single phase of CoCu₅Sn₅, the original phase, or the mixed phases of Cu₆Sn₅ and Co or Co-Sn alloys, we compared carefully the diffraction patterns of Cu₆Sn₅ and CoCu₅Sn₅ after the first cycle with those of as-prepared Cu₆Sn₅ and CoCu₅Sn₅ as shown in Fig. 5, the enlarged figure of Figs. 4A and 4B around 30°. The result showed that the recharged product can be indexed to a CoCu₅Sn₅ phase evidenced by the diffraction peak of 30.1°, not the Cu₆Sn₅ phase with the signature diffraction peak of 29.9°

Finally, the Co₂Cu₄Sn₅ electrode obviously proceeds in entirely different Li-ion alloying mechanisms from that of Cu₆Sn₅ and CoCu₅Sn₅ as shown in Fig. 4C. We do not find any trace of Li₂CuSn or $Li_2Co_vCu_{1-v}Sn$ at the discharge state of 180 (0.12 V) and 230 mAh/g (0.1 V) (curves b and c of Fig. 4C). It seems that the Co₂Cu₄Sn₅ transforms directly to Li_xSn and does not undergo the intermediate phase of Li2CovCu1-vSn upon the first discharge process. The peaks of Li_xSn become strong when the cell reaches to 0.0 V (curve d of Fig. 4C). Also, the coexistences of two- or threephase, the original Co₂Cu₄Sn₅, lithiated Li₂Co_yCu_{1-y}Sn, and Li_ySn phase was not detected when the cell was charged to 400 mAh/g at 0.65 V, as shown in curve e of Fig. 4C. We cannot obviously exclude the possibility of the existence of intermediate phases of Li₂Co_vCu_{1-v}Sn as the XRD intensity becomes too weak to be detected in the ex situ XRD experiment due to low crystalline with the increasing amounts of Co. When the cell reaches 1.5 V, the Li_xSn identified by the peaks around 23° also exists in the fully charged



Figure 6. The calculated relative energy and cell volume per formula unit of (a, b) $Co_x Cu_{6-x}Sn_5$ (x = 0, 1, 2, 3, 4, 5, and 6) and (c, d) $Li_2Co_yCu_{1-y}Sn$ (y = 0.00, 0.25, 0.75, and 1.00).

states, which can be attributed to the cleavage of Li_xSn with the current collector. The signature peaks of the $Co_2Cu_4Sn_5$ were almost not detected; only a very weak peak at 31.5° was observed which can be considered the unreacted $Co_2Cu_4Sn_5$. While no diffraction peaks of crystalline Sn, Cu, or Co were observed in the recharged product, there are still two possibilities. The first possibility is that the Co, Cu, and Sn exist in low-crystalline or amorphous states beyond the X-ray detection, and the second is the formation of amorphous or low crystalline $Co_2Cu_4Sn_5$. As pointed out above, by comparing the shapes of the charge curve of the first cycle with that of the tenth cycle, it still keeps the original shape. Furthermore, the three distinguished charge plateaus, a signature of Li-ion insertion in pure Sn alloy, were not observed on the tenth cycle. Therefore, we conclude that the product of the recharged $Co_2Cu_4Sn_5$.

Solid solution of $Co_xCu_{6-x}Sn_5$ and $Li_2Co_yCu_{1-y}Sn$.— In order to predict the crystal structure and thermodynamic stability of the $Co_xCu_{6-x}Sn_5$ and the metastable phase of $Li_2Co_yCu_{1-y}Sn$, we applied the first-principles calculation based on the density-functional theory with pseudopotentials and plane wave basis (VASP). We defined the relative energy of $Co_xCu_{6-x}Sn_5$ and $Li_2Co_yCu_{1-y}Sn$ as the following functions

$$E_f^1 = E_{\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5} - (6 - x)E_{\text{Cu}_6 \text{Sn}_5} - xE_{\text{Co}_6 \text{Sn}_5}$$
[4]

$$E_f^2 = E_{\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}} - (1-y)E_{\text{Li}_2\text{CuSn}} - yE_{\text{Li}_2\text{CoSn}}$$
[5]

where E_f^1 and E_f^2 are the relative energies of $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$ and $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$ and E_{C} is the total energy of compound C. The relative energy and volume per formula unit of $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$ are shown in Fig. 6a and b. We can see that the relative energy of $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$ is negative with respect to the sum of energies for $(6 - x)\text{Cu}_6\text{Sn}_5$ and $x\text{Co}_6\text{Sn}_5$, suggesting that it is possible thermodynamically that the $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$ form a homogeneous solid matrix in a unit cell level rather than a simple mixture of Cu_6Sn_5 and Co_6Sn_5 crystals in the ratio of (6 - x) to x.²¹ The cell volume per formula unit decreases with increasing amounts of Co in $\text{Co}_x\text{Cu}_{6-x}\text{Sn}_5$, as shown in Fig. 6b. This is in good agreement with the results of XRD and the Rietveld refinement. In the case of $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$, the similar phenomenon is observed from Fig. 6c and d. It is also very likely that the $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$ form a nimple mixture of Co_xSn_5 form a homogeneous solid matrix in a unit cell level rather than a simple mixture of Co_xSn_5 and Co_6Sn_5 .

Li₂CuSn and Li₂CoSn crystals in the ratio of (1 - y) to y during the charge and discharge process. The cell volume per formula unit also decreases with increasing amounts of Co in Li₂Co_yCu_{1-y}Sn.

Average voltage and possible reaction path.— The calculated average Li alloying reaction voltage of $Co_y Cu_{1,2-y} Sn$ (y = 0.0, 0.25, 0.75, and 1.00), V_1 ($0 \le \text{Li} < 2$), V_2 ($2 \le \text{Li} \le 4.4$), and V_3 (0 \leq Li \leq 4.4) are shown in Table III. The calculated average voltage of undoped Cu-Sn alloy, 0.451 V during Li content from 0 to 4.4, is higher than the previous report of 0.378 by Sharma et al.⁸ despite the different crystal structure used in the calculation, and it is also higher than the experimental value in the voltage profile (see Fig. 7 for the second discharge profile). The difference between the voltage of first-principles calculations and electrochemical experiments may be due to the systematic overestimating which is in part because the product phase is nucleated under stress in the matrix of the original compound or metal, whereas the calculations treat the product as stress free.²² We also note that the average voltage calculated in the manner described above is a bulk equilibrium quantity and does not contain contributions from the cathode surface, kinetic phenomena, or thermal entropies (the latter is expected to have only an extremely small effect on average voltage).²³ Although the systematic overestimating between the calculated average voltage and the experimental value exists, the voltage change tendency along with the increase in doped Co content is reliable. We can see from Table III that the average voltage decreases first during the discharge process of $0 \le Li \le 2$, then increases during $2 \le Li \le 4.4$, with increasing amounts of Co in Co_vCu_{1.2-v}Sn. The total average voltage during $0 \le Li \le 4.4$ decrease with increasing amounts of Co in

Table III. Reversible electrode potentials vs Li/Li⁺ estimated by the first-principles calculation for the Co-doped alloys.

	Average voltage vs Li/Li ⁺ for Co _y Cu _{1.2-y} Sn						
	$V_1 \ (0 \le \text{Li} < 2)$	$V_2 \ (2 \le \text{Li} \le 4.4)$	$V_3 \ (0 \le \text{Li} \le 4.4)$				
у	(V)	(V)	(V)				
0.00	0.719	0.227	0.451				
0.25	0.661	0.237	0.430				
0.50	0.593	0.279	0.430				
0.75	0.527	0.319	0.413				
1.00	0.469	0.351	0.405				



Figure 7. The 2nd discharge curves of Li/alloy cells containing $Co_xCu_{6-x}Sn_5$ alloys at a current of 0.25 mA/cm² at 2nd cycle: (a) Cu_6Sn_5 , (b) $Co_{0.5}Cu_{5.5}Sn_5$, (c) $CoCu_5Sn_5$, and (d) $Co_2Cu_4Sn_5$

 $Co_yCu_{1,2-y}Sn$. This is in good agreement with the tendency of the experimental discharge profiles as shown in Fig. 7

Because alloys with different Co content have different charge/ discharge profiles and lithium alloying mechanisms as shown in the ex situ XRD experiment, we studied the possible reaction path base on the first-principles calculation as already done in the previous report for the alloys of InSb and Cu₂Sb.²⁴ Here, we just consider the three charge/discharge states as mentioned above and we determine the formation energies for various lithiated products of Co_xCu_{6-x}Sn₅ [presented here by Co_yCu_{1.2-y}Sn (y = 0, 0.25, 0.5, and 0.75)] using the following formula

$$\begin{split} \text{Li}_x \text{Co}_y \text{Cu}_z \text{Sn} + (4.4 - x)\text{Li} \to \text{Li}_{4.4}\text{Sn} + y\text{Co} + z\text{Cu} \\ (0 \le x \le 4.4, 0 \le y \le 1.2, 0 \le z = 1.2 - y \le 1.2) \quad [6] \end{split}$$

The formation energy for the compound $\text{Li}_x \text{Co}_y \text{Cu}_z \text{Sn}$ is

 $\Delta E = E_{\text{Li}_{x}\text{Co}_{v}\text{Cu}_{z}\text{Sn}} + (4.4 - x)E_{\text{Li}} - (E_{\text{Li}_{4.4}\text{Sn}} + yE_{\text{Co}} + zE_{\text{Cu}})$ [7]

Here E_C is the total energy of the compound C or the energy per atom for metallic C. The formation energy defined this way reflects the relative stability of the compound Li_xCo_yCu_zSn with respect to the fully lithiated products of Li_{4.4}Sn and metal Co and Cu. These formation energies for Co_yCu_{1.2-y}Sn and its lithiated products are presented in Fig. 8. As can be seen the formation energy becomes



Figure 8. The calculated formation energy of unlithiated alloys, $Co_yCu_{1,2-y}Sn$, half lithiated states, $Li_2Co_yCu_{1-y}Sn$ (y = 0.00, 0.25, 0.75, and 1.00), and full lithiated states, $Li_{4,4}Sn$, calculated according to Eq. 6.



Figure 9. Partial electronic density of states for $Li_2Co_yCu_{1-y}Sn$ (y = 0, 0.25, and 0.75): (a) Li_2CuSn , (b) $Li_2Co_{0.25}Cu_{0.75}Sn$, and (c) $Li_2Co_{0.75}Cu_{0.25}Sn$.

gradually lower during the lithium alloying reaction, i.e., the lithiation reaction is spontaneous. The formation energy of the original unlithiated alloys decreases with the increasing amount of Co with respect to the full lithiated states, indicating a decrease in the total energy released during discharge, and a decrease tendency of the average voltage. The formation energy of the intermediate metastable phases of Li₂Co_vCu_{1-v}Sn become higher when Co content increases, suggesting that they become unstable. This finding is in accordance with the above analysis in the ex situ XRD experiment results. Based on the fact of the ex situ experiments and the calculated formation energy of the intermediate phase, we speculate the lithiation reaction paths may occur in the following ways. When small Co-doped in the Cu₆Sn₅, the formation energy of the intermediate phases of Li₂Co_vCu_{1-v}Sn has a small rise compared with the undoped counterparts as shown in curve b of Fig. 8 and therefore there is no obvious change in the reaction path with respect to the Cu₆Sn₅. However, with the increased amount of Co content in the $Co_x Cu_{6-x} Sn_5$, the intermediate phases of $Li_2 Co_y Cu_{1-y} Sn$ became unstable and transform quickly to the final product as soon as they appear. As a result, it is hard to detect in the ex situ XRD experiment. This makes it reasonable for the three-phase coexistence phenomenon observed in our ex situ XRD experiments. Finally, when the Co content reaches to the level of 1/3, the alloys may not undergo the intermediate phases of Li₂Co_vCu_{1-v}Sn but transform directly to the full lithiated states of Li4.4Sn and the metal matrix of Co and Cu.

Electronic density of state.— In order to investigate the relationship between the cycle performance and electronic structure, we calculate the partial electronic density of states of $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$ (y = 0, 0.25, and 0.75) using the first-principles method. Figure 9 shows the partial electronic density of states for $\text{Li}_2\text{Co}_y\text{Cu}_{1-y}\text{Sn}$ (y = 0, 0.25, and 0.75). The Sn 5p orbital and Cu 3d orbital provide the overlap. Such overlap has been strengthened when Cu is substituted partially by Co, as indicated by the appearance of the broad



Figure 10. The electron density difference between lithiated and unlithiated alloys in the Millar plane of (110): (A) Li₂CuSn and (B) Li₂CoCuSn. The difference is given in charge per a^3 , and darker indicates larger electron density.

peak at about -1.8 eV. So, the Cu-Sn part of the crystal structure, the host of lithium ions, may become more stable. However, we supposed that when the substitution comes to the high level, the Co-Sn part of the crystal structure becomes the main host of lithium ions, and it provides an unstable host for the lithium-ion because the orbital overlap between the Sn 5p and Co 3d is much weaker than that of Sn 5p and Cu 3d, as shown in Fig. 9. Therefore, some certain level of Co substitution of Cu in $Li_2Co_yCu_{1-y}Sn$ may be preferable for avoiding the pulverization of (the stability of) the crystal structure, thus resulting in good cycling performance.

Valence charge density.— Figure 10 compares the valence charge density between Li₂CuSn and Li₂CoCuSn. These results are obtained by subtracting the charge density in Li₂CuSn from that in CuSn and Li2CoCuSn from that in CoCuSn. For the calculations of CoCuSn, we used the Co-Cu-Sn part of the crystal structure of Li2CoCuSn, which means all atomic positions were assumed to remain unchanged on the structure of Li2CoCuSn (however, for the voltage calculations, all coordinates were fully relaxed and the hexagonal $Co_x Cu_{6-x} Sn_5$ structures were used for the unlithiated alloys). The Millar plane of (110) has been chosen to facilitate direct comparison with the previous work⁸ and for clarity in showing all atoms. From Fig. 10A, we could observe that the increased electrons in Cu_{1.2}Sn along with the insertion of lithium were distributed mostly in a narrow band area between Sn/Cu and Li atoms. The electron charge was well deformed and the structure shows a relative metallic character. In the case of Co-substituted Cu-Sn alloy, Co accepts some charge from the extra lithium atoms and the charge density of the band area is lower than that of the nonsubstituted alloy. Furthermore, a comparison of Fig. 10A and 10B indicates that Li2CoCu shows a more spherical shape of charge distribution, which means a more ionic character of the bonds according to Edström.⁸ In a word,

the lithiation of high-level Co-substituted Cu-Sn alloy results in a charge transfer from Li to the Co atoms to form the more ionic LiCoCuSn phase, which is more likely to be pulverized upon cycling and thus lead to a poorer cycle performance.

Conclusion

Co-doped $\text{Co}_x \text{Cu}_{6-x} \text{Sn}_5$ ($0 \le x \le 2$) alloys show the same structure but different electrochemical performance with Cu₆Sn₅ as the anodes of Li-ion batteries. A proper amount of Co-doped alloy, CoCu₅Sn₅, showed improved cycling stability at the expense of capacity, whereas a heavy Co-doped alloy, Co₂Cu₄Sn₅, resulted in poor cycling ability. The first-principles calculations suggest that a certain level of Co substitution of Cu in Co_xCu_{6-x}Sn₅ may be preferable for avoiding the pulverization of the crystal structure, thus resulting in good cycling performance. It was found that metastable intermediate phases of Li2CovCu1-vSn form during the Li-ion alloying process and became unstable and even undetectable with increasing amounts of Co substituted in Co_xCu_{6-x}Sn₅ by ex situ XRD analysis and first-principles calculation. The full electrochemical reaction of lithium with Co_rCu_{6-r}Sn₅ leads to a mixed phase of the disordered Li_{4.4}Sn and metal Co and Cu, and the initial intermetallic alloys are reformed when lithium was extracted from the alloys during charge.

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