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Rapid fabrication of tin-copper anodes for lithium-ion battery applications

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Abstract

The intermetallic Cu₆Sn₅ is ubiquitous in electronic interconnects where research has focused on controlling the size and distribution of this phase for improved performance. Cu₆Sn₅ also

finds application as an anode material for advanced lithium-ion batteries. Cu_6Sn_5 anodes can be fabricated via an in-situ growth method involving the reaction between molten Sn and the Cu current collector. This manufacturing route offers some advantages over traditional anode fabrication however the process is slow, limiting its practical application. In this work we show the addition of 6 wt% Ni to the Cu current collector greatly accelerates the growth of $(\text{Cu,Ni})_6\text{Sn}_5$ in Cu-xNi/Sn solid-melt couples, leading to a growth rate of up to 50x faster, reducing the processing time above 200°C to less than 10 minutes. This research studies the dynamics of the formation of $(\text{Cu,Ni})_6\text{Sn}_5$ between Cu-xNi alloys and liquid Sn through real-time observation using synchrotron X-ray imaging. The $(\text{Cu,Ni})_6\text{Sn}_5$ growth dynamics are characterised, and the growth kinetics are analysed. Subsequently, the mechanism of the accelerated growth is investigated with electron backscatter diffraction and transmission electron microscopy. The results show the accelerated growth is due to the formation of η - $(\text{Cu,Ni})_6\text{Sn}_5$ grains with two distinct Ni concentration ranges, leading to finer grains and spalling, which in turn facilitates the diffusion of Sn, enhancing the η - $(\text{Cu,Ni})_6\text{Sn}_5$ formation kinetics.

1 Introduction

Li-ion batteries (LIBs) have found numerous applications in modern technologies, especially in portable devices, electric vehicles and renewable energy storage. However, LIB fires and explosions due to the formation of Li metal dendrites on carbon-based anodes, along with the constant demand for higher energy density, are motivating a move away from traditional carbon-based anodes. The intermetallic compound (IMC) Cu_6Sn_5 is a promising candidate anode material due to the high theoretical storage capacity of Sn at 993 mAh g⁻¹ in comparison with commercial graphite anodes at 372 mAh g⁻¹, combined with a better

cycleability compared to pure Sn [1, 2], and a higher lithiation potential of around 0.4 V vs. Li/Li⁺ [2, 3], decreasing the likelihood of Li dendrite formation.

Traditional LIB anode manufacturing is a multi-steps process, involving the preparation of the active Cu₆Sn₅ material, mixing the active material with binders and conductive materials to form a slurry, slip casting the slurry on the current collector, and finally evaporating the solvents to obtain the anode. A simplified method for manufacturing Cu₆Sn₅ anodes via in-situ formation of Cu₆Sn₅ on the Cu current collector has been recently proposed, taking advantage of a process that commonly occurs at the interface between the Cu substrate and a number of Sn-based solder alloys [3, 4]. When a Cu/Sn couple is heated above the melting point of Sn, Cu₆Sn₅ is formed spontaneously at the solid/melt interface (Fig. 1a). The resultant anode is found to achieve a capacity of up to 929 mAh g⁻¹ at a charge/discharge rate of C/7, and retaining up to 480 mAh g⁻¹ at 2C [5]. However, the growth rate of Cu₆Sn₅ is slow, where only a few micrometres of Cu₆Sn₅ is grown in hours, presenting a major hurdle for commercial production using this method.

The addition of Ni to the Cu current collector greatly accelerates the growth of (Cu,Ni)₆Sn₅ [6-16], and this study investigates this method for the potential to significantly shorten the fabrication time of (Cu,Ni)₆Sn₅ anodes. The growth dynamics are characterised by in-situ synchrotron transmission X-ray imaging where the formation sequence of (Cu,Ni)₆Sn₅ is observed in real-time. The X-ray radiographs are also analysed to obtain the real-time growth kinetics. In addition, the combined results of scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and spherical aberration corrected scanning transmission electron microscopy (C_s-corrected STEM) reveal the mechanisms of the rapid growth.

Fig. 1. SEM cross-section micrographs showing the layer of Cu_6Sn_5 grown at 240°C for 15 minutes. Cu_6Sn_5 grown between Sn and **a**, a pure Cu foil and **b**, a Cu-6Ni foil. Higher magnification images of the interfaces with **c**, Cu showing Cu_3Sn and **d**, Cu-6Ni showing no Cu_3Sn .

2 Experimental

2.1 Anode fabrication. The $(\text{Cu,Ni})_6\text{Sn}_5$ anodes were fabricated by an in-situ growth method where the $(\text{Cu,Ni})_6\text{Sn}_5$ IMCs were formed directly on a Cu-based current collector [3]. A Sn (99.9%, cast and rolled, ingots supplied by Northern Smelters Pty Ltd., Australia) and a Cu-xNi (99.9%, cast and rolled, sheets supplied by Shanghai Husheng Precision Hejin Limited Company, China), where $x = 0$ and 6 wt%, were clamped together between two glass slides with a metal clip to form a Cu-xNi/Sn couple. Soldering flux Weldwell 509 was applied between the two sheets to remove surface oxides. The couple was placed in a preheated oven at 240°C for 15 minutes. The thickness of the Sn and Cu sheets varied depending on the requirements of the experiments and high temperature polymer foil spacers were used to control the thickness of the Sn melt:

- To demonstrate the rapid growth and that a Sn-free dense layer of $(\text{Cu,Ni})_6\text{Sn}_5$ can be obtained, Cu-xNi foils of $30\ \mu\text{m}$ and a molten Sn layer (polymer spacer) of $50\ \mu\text{m}$ were used.

- To study the growth mechanism, 1 mm thick Sn and Cu-xNi foils were used to observe the microstructure and distribution of $(\text{Cu,Ni})_6\text{Sn}_5$ in the Sn melt.

The samples were then allowed to cool to room temperature in air, and rinsed in ethanol. Residual Sn for the working anode was removed by chemical dissolution in a 1.75 g ortho-nitrophenol, 2.5 g sodium hydroxide and 50 ml water solution at 80°C. The residual Sn in most of the microscopy samples was not removed as it helps to protect the IMCs during mechanical polishing, an exception being where Sn was selectively dissolved after polishing to reveal the three-dimensional structure of the IMCs.

2.2 Material characterisation. The samples were mounted in resin and standard metallography procedures were used to prepare the samples for cross-section SEM observation, followed by ion-milling to remove surface stresses before the EBSD study. The EDS results were obtained by averaging point analysis data from 10 different $(\text{Cu,Ni})_6\text{Sn}_5$ grains for each point plotted for the dense and porous layers. The data plotted at a 300 μm distance from the Cu-6Ni interface is obtained by averaging point analysis data from the Sn-rich area from 300 – 1000 μm , at a height interval of 100 μm , with 3 point analyses at each height interval ($8 \times 3 = 24$ point analyses in total). Note that the data has a variance of ± 0.2 wt% Ni.

The TEM lamellar was prepared by a focused ion-beam (FIB) technique described elsewhere [17], and thinned by an ion mill at 900 eV to a thickness of about 50 nm for electron transparency, before imaging and EDS in a C_s -corrected STEM at 200 kV accelerating voltage. The TEM selected area electron diffraction (SAED) patterns were also obtained.

Fig. 2a depicts the beamline setup for in-situ synchrotron X-ray imaging, with the sample placed in the furnace covered in a chamber to minimize air convection and temperature fluctuation, and a beam monitor placed on the X-ray beamline. The Cu-6wt%Ni (Cu-6Ni

hereafter) and Cu current collectors, along with a 99.9% Sn sheet were rolled and ground to approximately 100 μm in thickness. The substrates were cut to approximately 4 x 6 mm in width and length, while the Sn sheet was cut to pieces of approximately 1 mm x 6 mm in width and length. The sample cells (Fig. 2b) were made from 2 x 50 μm thick polytetrafluoroethylene (PTFE) sheets sandwiched in between two quartz plates of 1 mm in thickness. The PTFE sheets were cut to create a cavity for the Cu-6Ni/Sn sample (dimensions of the specimen were approximately 5 x 6 mm) and a 2.5 mm wide channel centrally placed at one side of the cell. The substrate and the Sn sheet were placed in contact with each other in the sample cell with flux applied to the sample to remove oxides. The sample cell was then inserted into a graphite resistance furnace mounted on the BL20XU beamline at the SPring-8 synchrotron for the observation of the $(\text{Cu,Ni})_6\text{Sn}_5$ growth.

The sample cell was heated at a rate of 10°C per minute from room temperature to 150°C, and then 5°C per minute to 240°C to prevent overshoot. To avoid the thermocouple from obstructing the imaging, it is positioned away from the X-ray beam, which results in a difference in the measured temperature and the actual temperature experienced by the sample. The thermocouple was calibrated by observing the melting point of the sample (pure Sn at 232°C), and the measured and actual temperature profiles are approximated in Fig. 2c. The sample was then held at 240°C for 15 minutes for $(\text{Cu,Ni})_6\text{Sn}_5$ growth, before the heater was switched off to allow the sample to cool to room temperature by natural convection. In-situ X-ray video of the IMC formation was recorded simultaneously. In addition, 128 frames of direct beam images and dark images were taken to remove backgrounds from the experimental setup and the beam monitor during image processing. The beam energy was monochromatized to 21 keV, and the observation area was set to 1 x 1 mm. A beam monitor with pixel size of 0.5 x 0.5 μm , which consisted of a fluorescent screen and a CMOS-type camera, was used, and images were captured at a frame rate of 1 frame per second (fps).

2.3 Thickness measurement and image processing. The synchrotron radiographs were analyzed with a combination of Matlab (Mathworks, Natick, MA, USA) and Fiji ImageJ [18]. First, flatfield corrected image sequences were shift-corrected by selecting the $(\text{Cu,Ni})_6\text{Sn}_5/\text{Cu-6Ni}$ interface as a reference using “align slices in stack” plugin [19] in Fiji ImageJ. To track the movement of the $(\text{Cu,Ni})_6\text{Sn}_5$ growth front, a routine was written in Matlab to identify the frame for which each pixel that was originally liquid Sn becomes a solid. Locally weighted linear regression was applied for smoothing the noise of transmission intensity in time, and the sudden change in the intensity associated with the arrival of the $(\text{Cu,Ni})_6\text{Sn}_5$ growth front was defined by the intersection between a horizontal line representing the average intensity of liquid tin prior to solidification and a linear-fit line through the point with steepest slope. The average thickness was derived from the area of porous $(\text{Cu,Ni})_6\text{Sn}_5$ layer divided by the width of the observation area (1 mm), and was plotted against holding time to investigate the porous layer growth kinetics.

Fig. 2. In-situ synchrotron X-ray imaging experimental setup. Schematic of **a**, the in-situ X-ray imaging experimental setup and **b**, the sample cell configuration. **c**, A plot of the approximated actual and measured temperatures during video recording.

2.4 Validation of electrochemical reactivity. It has previously been established that the reaction of Sn with a substrate that contains both Ni and Cu results in the formation of

(Cu,Ni)₆Sn₅ rather than Cu₆Sn₅, however, the electrochemical reactivity of this compound has not been validated. Therefore, although this paper is primarily focused on improving the manufacturing process, it was considered important to confirm that the presence of Ni in (Cu,Ni)₆Sn₅ did not adversely affect the lithiation/delithiation reactions. The reactivity of the electrode was tested by lithiating/delithiating the sample between 0.02-1.20 V, and the reactions were characterised by synchrotron powder X-ray diffraction (PXRD). The growth temperature was lowered to 232°C and the growth time was shortened to 7 minutes to produce a layer of (Cu,Ni)₆Sn₅ of 7 µm in thickness on a working anode for lithiation. The (Cu,Ni)₆Sn₅ anodes were assembled into 2032 coin cells with Li as counter electrodes and 1 M LiPF₆ in EC/DMC 50:50 as an electrolyte. For the synchrotron PXRD experiment, windows of 5 mm in diameter, sealed with polyimide tape, were incorporated on each side of the coin cells to allow the transmission of an X-ray beam. The coin cells were pre-lithiated to the following charge states: i. fresh, ii. 0.30 V, iii. 0.20 V, iv. 0.13 V, v. 0.10 V, vi. 0.05 V, vii. 0.02 V and delithiated to viii. 1.00 V (1 cycle) at a low current of 0.03 mA cm⁻² before the PXRD data was collected with an in-house setup [20]. The X-ray beam energy was conditioned to 16 keV, giving a refined wavelength, λ of 0.07734 nm obtained from a LaB₆ 660c NIST standard.

3 Results and discussion

3.1 IMCs thickness and Cu₃Sn suppression. When 30 – 50 µm thick Sn sheets are used in the Cu/Sn couple, at 240°C (above the liquidus of the Sn), only 4 µm of Cu₆Sn₅ is grown after 15 minutes on a pure Cu current collector, leaving a layer of residual Sn on top (Fig. 1a); while, under the same conditions, when 6 wt% of Ni is present in the Cu current collector, the interfacial reaction is greatly accelerated (in-situ study shows a 50 times thicker IMC layer) and the Sn is fully consumed in the reaction, forming a dense layer of (Cu,Ni)₆Sn₅ that is 60 µm thick (Fig. 1b).

Furthermore, with the presence of Ni, Cu_3Sn does not form (Fig. 1c and d). This result is later confirmed by higher resolution observation under C_s -corrected STEM. The lack of Cu_3Sn at the Cu-6Ni/Sn interface is similar to the effects of Ni when it is present as an alloying addition in the Sn alloy instead of the Cu [21, 22]. Cu_3Sn does not react with Li as an active anode material at room temperature [23], decreasing the specific capacity of the electrode. Therefore, the suppression of this phase improves the efficiency of Li storage in the anode.

3.2 In-situ synchrotron X-ray imaging. To study the dynamics of the rapid growth, real-time observation of the growth of $(\text{Cu,Ni})_6\text{Sn}_5$ on a Cu-6Ni current collector was performed (Movie A.1, Supplementary material). For comparison, the growth of Cu_6Sn_5 on a Cu current collector under similar experimental conditions is also observed (Fig. 3). Synchrotron X-ray imaging has previously been used to study the formation of Cu_6Sn_5 between a number of Sn-based solder alloys and Cu substrates [24, 25], and the technique is adopted for this study using a frame rate of 1 fps. As the sample is heated to 240°C , the Sn sheet started to melt around 232°C at frame 1270 (Fig. 4a), and was completely molten at frame 1286 (Fig. 4b). During isothermal holding at 240°C , there is a period of approximately 100 s before a thin layer of $(\text{Cu,Ni})_6\text{Sn}_5$ was observed at the solid/melt interface. The $(\text{Cu,Ni})_6\text{Sn}_5$ started to grow rapidly (compared with binary Cu/Sn) from frame 1460, as can be observed in Fig. 4c-e as the sample was held at 240°C for 15 minutes. At frame 2240, an average thickness of $200\text{ }\mu\text{m}$ was obtained. The thickness of the $(\text{Cu,Ni})_6\text{Sn}_5$ layer was quantified (Fig. 5a).

At the end of the 15 minutes at 240°C (frame 2240 s), the heater was switched off and the sample was allowed to cool to room temperature in air. Needle-like IMCs started to form in the Sn-rich melt around frame 2278 (Fig. 4f) and these IMC needles continued to nucleate and grow during cooling (Fig. 4g). Fig. 4h is a magnified view of the area framed in red in Fig. 4a to depict the IMC needles at frame 2281.

Fig. 3. Real-time X-ray imaging of reactions between Cu and Sn at the solid-melt interface. Images taken at IMC growth times **a**, 10 s, **b**, 300 s, **c**, 600 s and **d**, 851 s. Growth time starts when the Sn is fully molten.

Fig. 4. Real-time X-ray imaging of reactions between Cu-6Ni and Sn at the solid-melt interface. Images at video frames (growth times) **a**, 1270 (-16 s), **b**, 1286 (0 s), **c**, 1460 (174 s), **d**, 1850 (564 s), **e**, 2240 (954 s), **f**, 2278 (992 s), **g**, 2950 (1664 s) and **h**, a magnified image of the red framed area in **a**, at frame 2281 (995 s), with the blue arrows pointing out the $(\text{Cu,Ni})_6\text{Sn}_5$ formed upon cooling. Large bubbles pointed out by the red arrows in **b**, are flux bubbles, while the small bubbles pointed out by the green arrows are air trapped by a PTFE layer on the sample cell.

3.3 Interface IMC growth rates. The average thicknesses of the IMC layer for each frame and time, analysed by Matlab and Fiji ImageJ, are listed in Spreadsheet A.1 and A.2, Supplementary material, for the Cu/Sn and Cu-6Ni/Sn datasets respectively. The interfacial

growth of IMCs as seen in Fig. 5a is often characterised by the parabolic growth equation $h = kt^n$, where h is the thickness of the $(\text{Cu,Ni})_6\text{Sn}_5$ layer in μm and t is time in seconds, and k and n are the growth constants [26]. The growth curve in Fig. 5a can be divided into two sections, where parabolic growth is observed from growth time, t between 0 to 200 s, followed by a transition to linear growth from $t = 200$ s onwards. There is an initial period of accelerating growth rate which can be fitted with $k = 1/90$ and $n = 1.4$, resulting in a R^2 value of 0.9997; while the linear growth region can be represented by a linear fit: $h = 0.24t - 33$, with an R^2 value of 0.9996 (Fig. 5a). The linear fit implies that $n = 1$ for the Cu-6Ni/Sn couple, suggesting that the growth rate of $(\text{Cu,Ni})_6\text{Sn}_5$ is independent of the layer thickness, as opposed to the volume diffusion controlled ($n = 0.5$) growth reported for the formation of Cu_6Sn_5 between Sn and pure Cu [26].

3.4 Microstructure and composition. Due to the difficulty in metallographic preparation of the thin X-ray imaging sample, a sample replicating the conditions in the in-situ X-ray imaging experiment was fabricated in the laboratory. Cross-section SEM of this sample revealed a microstructure similar to the in-situ X-ray images (Fig. 5b). Imaging close to the Cu-6Ni interface shows a dense layer of IMC of about 4 μm thick adjacent to the Cu-6Ni, while the IMC layer above, between 150-200 μm in thickness, is porous, consisting of a $(\text{Cu,Ni})_6\text{Sn}_5$ skeleton filled with Sn (Fig. 5b and c). The porous layer appears wave-like with multiple sub-layers (Fig. 5b and c).

Fig. 5d shows the SEM energy dispersive X-ray spectroscopy (EDS) results of wt%Ni in $(\text{Cu,Ni})_6\text{Sn}_5$ vs. distance from the Cu-6Ni interface. The individual EDS data which provided this averaged result is collated in Table B.1 and B.2, Supplementary material. The data shows that Ni is uniformly distributed in the Cu-6Ni plate, with an average composition of 6.8 wt%Ni, and a standard deviation of 0.3 wt%Ni. Considering $(\text{Cu,Ni})_6\text{Sn}_5$ is composed of approximately 54.5 at%(Cu +Ni) and 45.5 at%Sn, a Cu:Ni weight ratio of 94:6 as in the Cu-

6Ni foil should result in approximately 3.5 at%Ni (2.3 wt%Ni) in $(\text{Cu,Ni})_6\text{Sn}_5$ when homogeneously reacted, i.e. when Cu and Ni atoms dissolve and diffuse in liquid Sn at the same rates. Since the distribution of Ni in Cu-6Ni is considered homogeneous, the dissolution rates of Cu and Ni shall be in the ratio of 94:6 wt%. The amount of Ni in the dense layer which averages around 3.1 wt%Ni (Fig. 5d), is higher than the 2.3 wt%Ni stoichiometry, suggesting Sn preferentially reacts with Ni compared to Cu to form $(\text{Cu,Ni})_6\text{Sn}_5$. The $(\text{Cu,Ni})_6\text{Sn}_5$ Ni content in the porous layer adjacent to the dense/porous interface is very close to 2.3 wt% and increases almost linearly to 3.7 wt% at 200 μm from the Cu-6Ni interface. In contrast, the $(\text{Cu,Ni})_6\text{Sn}_5$ crystals precipitated from the Sn-rich melt during cooling have very low Ni contents, averaging at 0.3 wt%Ni. The inhomogeneous distribution of Ni suggests a higher diffusion rate of Cu, i.e. Cu tends to diffuse further away from the interface compared to Ni upon dissolution. The formation of $(\text{Cu,Ni})_6\text{Sn}_5$ with lower Ni concentration during the later stages of solidification at lower temperatures may also have contributions from the lower solubility limit of Ni in $(\text{Cu,Ni})_6\text{Sn}_5$ at lower temperatures [27, 28].

Fig. 5. IMC growth rates, microstructure and Ni content. a, Thickness of the $(\text{Cu,Ni})_6\text{Sn}_5$ IMC layer vs. time in contact with molten Sn for the Cu-6Ni/Sn and Cu/Sn couples. Cross-section SEM image of a Cu-6Ni/Sn couple, showing b, the Cu-6Ni, interface IMC layers and

the Sn rich area, **c**, magnified view of the interface IMC layers. **d**, SEM-EDS results showing wt%Ni in $(\text{Cu,Ni})_6\text{Sn}_5$ vs. distance from the Cu-6Ni interface.

TEM-EDS shows two heterogeneous compositions in the $(\text{Cu,Ni})_6\text{Sn}_5$ grains, with smaller grains in the dense layer, typically <100 nm in size, having higher Ni contents (Fig. 6a). Ni segregation is also found close to the Cu-6Ni interface (Fig. 6b), with a Ni-rich band observed adjacent to the Cu-6Ni. The selected area electron diffraction (SAED) patterns confirm that both the high Ni and low Ni grains are the hexagonal η - $(\text{Cu,Ni})_6\text{Sn}_5$ (Fig. 6c and d), which is known to be stabilised at room temperature by the presence of Ni [29, 30]. The η - Cu_6Sn_5 polymorph is preferred in LIB anode applications as it has larger and more open channels to facilitate Li-ion transport compared to the room temperature η' - Cu_6Sn_5 polymorph [31].

Confirming the SEM observation, no Cu_3Sn is visible in Figure 6b. Vuorinen et al. predicted the diffusion of Cu is via the formation of $\text{Cu}-(\text{Ni,Cu})_3\text{Sn}-(\text{Ni,Cu})_3\text{Sn}_2-(\text{Cu,Ni})_6\text{Sn}_5-\text{Sn}$ and this leads to the instability of the Cu_3Sn phase [32]. However, these layers were not observed in their study due to the limitation of FE-SEM [32]. The EDS map in Fig. 6b clearly show a Ni rich band at the Cu-6Ni interface, supporting Vuorinen et al.'s hypothesis that this may be the reason that Cu_3Sn does not form when a sufficient amount of Ni is in the system. Fig. 6b also shows no Ni segregation within the Cu-6Ni sheet itself.

Fig. 6. TEM microstructure, morphology and crystal structure of the $(\text{Cu,Ni})_6\text{Sn}_5$ electrode. TEM dark field (DF) image and EDS maps of the IMCs **a**, in the dense layer and **b**, at the Cu-6Ni interface. TEM SAED of **c**, a larger grain of lower Ni concentration and **d**, a smaller grain of higher Ni concentration (areas circled in red).

3.5 IMC morphology and grain sizes. Fig. 7a is obtained after selective etching of Sn from the sample cross-section, showing the dense/porous interface where a porous layer is partially attached to the dense layer. Pores at the top of the dense layer present evidence of the infiltration of liquid Sn along the $(\text{Cu,Ni})_6\text{Sn}_5$ grain boundaries during the early onset of spalling. Fig. 7b shows an overall view of the $(\text{Cu,Ni})_6\text{Sn}_5$ skeleton. The porous nature of the electrode and the less active $(\text{Cu,Ni})_6\text{Sn}_5$ compared to pure Sn can mediate the volume expansion of the electrode during cycling. It is clear from Fig. 7c, which shows the interface between the porous layer and the Sn-rich region (200 μm from the Cu-6Ni interface), that the $(\text{Cu,Ni})_6\text{Sn}_5$ grains have the shape of short rounded rods.

An EBSD phase map (Fig. 7d) of the cross-section before Sn is etched away confirms the presence of Sn at the $(\text{Cu,Ni})_6\text{Sn}_5$ grain boundaries where decohesion is observed, while inverse pole figure X-ray (IPF-X) maps are shown in Fig. 7e and f. The $(\text{Cu,Ni})_6\text{Sn}_5$ grains have a random orientation, as shown in the η' - Cu_6Sn_5 $\{001\}$, $\{100\}$ and $\{110\}$ pole figures in Fig. C.1a, Supplementary material.

The grain size was measured with both EBSD (Fig. 7f and Fig. C.1b, Supplementary material, grain size >300 nm, limited by EBSD pixel size) and TEM (Fig. 6b and Fig. D.1, Supplementary material, high resolution images of the local area close to the $(\text{Cu,Ni})_6\text{Sn}_5/\text{Cu-6Ni}$ interface), shows there is an increase in the grain size from the interface which has nano-grains below 100 nm, to around 500-600 nm at 15 μm away from the interface, and the average grain size stays constant beyond that. This also agrees well with the Rietveld refined average grain size in Table F.1, which will be discussed in the following sections. Many of the nano-grains adjacent to the Cu-6Ni interface have a columnar structure perpendicular to the Cu-6Ni current collector (Fig. D.1b).

Fig. 7. SEM and EBSD characterisation. a-c, SE-SEM images of the $(\text{Cu,Ni})_6\text{Sn}_5$ layers after selective etching of β -Sn. **a**, the Cu-6Ni substrate with a ~ 4 μm dense region of $(\text{Cu,Ni})_6\text{Sn}_5$ above, followed by porous $(\text{Cu,Ni})_6\text{Sn}_5$. **b**, Overall view of the interface

(Cu,Ni)₆Sn₅, showing sub-layers with different levels of porosity. **c**, (Cu,Ni)₆Sn₅ grains at the top of the layer. Note that ‘porosity’ was filled with β -Sn prior to etching and was liquid during growth of the IMC layer. **d**, EBSD phase map showing β -Sn (green) between many (Cu,Ni)₆Sn₅ grains (red). The FCC Cu-Ni phase is yellow. **e**, EBSD IPF-X map of Cu₆Sn₅ of the region in **d**. **f**, EBSD IPF-X map of Cu₆Sn₅ from a wider region at a lower magnification.

3.6 IMC formation mechanisms. It was suggested that the rapid growth of (Cu,Ni)₆Sn₅ on Cu-xNi is due to (i) the reduced solubility of Cu in the Sn melt with an increasing amount of Ni (phase diagram in [9]) which promotes the precipitation of Cu₆Sn₅ and (ii) the strong mutual interaction between the Cu, Ni and Sn atoms in the melt, causing the dissolved Cu and Ni to stay close to the solid-melt interface, as opposed to the pure Cu/Sn reaction where the Cu atoms can migrate further away from the interface, resulting in highly supersaturated Cu and Ni in the melt close to the interface, facilitating the formation of a thick (Cu,Ni)₆Sn₅ layer [9]. Furthermore, the volume diffusion flux of Sn in Cu₆Sn₅ also increases dramatically with the addition of Ni [32], though this is likely a secondary effect in solid-liquid Cu-xNi/Sn systems.

On the other hand, as the real-time observation suggests, a porous layer is formed at the solid/melt interface while the temperature is held at 240°C. The porous layer (Fig. 5b and c, 7a and b) enables a continuous supply of molten Sn close to the Cu-6Ni interface to react with Cu and Ni, therefore the diffusion of Cu and Ni through the (Cu,Ni)₆Sn₅ grains is no longer the rate limiting factor for the growth.

SEM images of the interface between the dense and porous IMC layers reveal areas where the porous sub-layer is attached to the dense layer (Fig. 5c), indicating that these sub-layers may be originally formed at the Cu-6Ni interface and then spalled off sub-layer by sub-layer with time. Multiple regions filled with Sn are also observed in the dense layer where it

connects with the porous sub-layers, showing evidence of the early stage where the layers begin to spall off.

The smaller grain size close to the $(\text{Cu,Ni})_6\text{Sn}_5/\text{Cu-6Ni}$ interface indicates that the $(\text{Cu,Ni})_6\text{Sn}_5$ grains continue to nucleate at this location instead of at the $(\text{Cu,Ni})_6\text{Sn}_5/\text{Sn}$ interface. This growth mechanism is very different to the growth mechanism of Cu_6Sn_5 formation in a Cu/Sn couple, where only a single layer of Cu_6Sn_5 grains are formed between Cu and Sn. Cu and Ni diffuse through the thin Ni-Sn IMC layer to react with Sn to nucleate and grow the high-Ni and low-Ni $(\text{Cu,Ni})_6\text{Sn}_5$ grains, while a portion of them diffuse through the $(\text{Cu,Ni})_6\text{Sn}_5$ layer and dissolve in Sn and continue to grow the $(\text{Cu,Ni})_6\text{Sn}_5$ IMCs. Some of the dissolved Cu and a relatively low amount of Ni proceed to diffuse away from the interface, eventually forming the low Ni $(\text{Cu,Ni})_6\text{Sn}_5$ grains in the Sn-rich area when the temperature is reduced (Fig. 4h).

Fig. 7d shows β -Sn between many of the individual Cu_6Sn_5 grains, indicating that the Cu_6Sn_5 grain boundaries decohered. This can be a consequence of the two heterogeneous grain compositions which lead to higher energy grain boundaries (GBs) as a result of impurity segregation as observed in many other metal systems [33-35], or GB melting [36]. GBs can melt to reduce the total interfacial energy if the boundary energy $\sigma_{\eta/\eta}$ is larger than twice of the IMC/liquid interface energy $\sigma_{\eta/L}$ [36]. $\sigma_{\eta/\eta}$ is approximated as 0.30 J m^{-2} , while $\sigma_{\eta/L}$ is likely between 0.1 to 0.15 J m^{-2} [37], which can satisfy the $\sigma_{\eta/\eta} \geq 2\sigma_{\eta/L}$ condition. Simulations showed the η grains do not coalesce at the lower $\sigma_{\eta/L}$ of 0.1 J m^{-2} [37]. Grain coalescence is also impeded with the high incoherence in the GB, resulting in the high Ni grains having smaller grain sizes. The proportion of low Ni grains is larger and the incoherence between these grains smaller, allowing them to coalesce to form the larger grains observed. The continuous spalling and retarded grain coalescence have also resulted in the much smaller grain sizes compared to the IMCs grown in a Cu/Sn system. This assumption of weaker GBs

describes the microstructure observed, though it is yet to be verified by direct experimental evidence.

Away from the Cu-6Ni interface, as seen in Fig. 4g and h, IMC needles continued to nucleate and grow during cooling. These $(\text{Cu,Ni})_6\text{Sn}_5$ needles are formed due to the reduced solubility of Cu and Ni in the melt as the temperature reduces.

This rapid growth mechanism is not observed in couples where Ni is added to the Sn alloys instead of Cu [29, 30]. In such couples, Ni is available at the top of the dense layer and IMC growth is likely to happen at the IMC/melt interface via the diffusion of Cu instead of at the Cu-xNi/IMC interface. This is demonstrated in a Cu-6Ni/Sn-0.7wt%Cu-0.05wt%Ni system [7], where the rapid growth is temporarily hindered when 0.05 wt% of Ni is added to the Sn melt, as the presence of Ni in the melt promotes a growth mode of IMCs at the IMC/melt interface, similar to the pure Cu/Sn-alloys systems.

3.7 Validation and characterisation of the electrochemical reactions. The lithiation voltage vs. normalised capacity curve of the anode for the ex-situ synchrotron powder X-ray diffraction (PXRD) and the comparable curve for an anode grown on a pure Cu current collector are presented in Fig. E.1, Supplementary material, validating the functionality of the $(\text{Cu,Ni})_6\text{Sn}_5$ electrode. Cu_6Sn_5 has a theoretical capacity of 5006 mAh cm^{-3} (based on un-lithiated Cu_6Sn_5). From the validation test, the 10 mm diameter x 7 μm thick $(\text{Cu,Ni})_6\text{Sn}_5$ electrode has a discharge capacity of 2.54 mAh, giving a specific capacity of 4620 mAh cm^{-3} , which is more than five times higher than the theoretical capacity of graphite anode at 840 mAh cm^{-3} . In other words, a $(\text{Cu,Ni})_6\text{Sn}_5$ electrode of around 9 μm in thickness would have an equivalent capacity to a commercial graphite anode of about 50 μm ($9 \mu\text{m} \times 4620/840$) thickness.

In Fig. E.1, the lithiation voltage plateaus of the η -(Cu,Ni)₆Sn₅ anode is very similar to the η '-Cu₆Sn₅ anode produced on pure Cu current collector [3], suggesting a similar two-step electrochemical reactions where Li first reacts with (Cu,Ni)₆Sn₅ to form Li₁₃(Cu,Ni)₆Sn₅, and as lithiation continues, proceeds to the second reaction where Cu and Ni separates from Li and Sn to form Li_(13+y)Sn₅ and (Cu,Ni). An exception is the (Cu,Ni)₆Sn₅ anode showed less solid-electrolyte interphases (SEIs) formation, as suggested by the more abrupt dip in voltage at the beginning of the lithiation process.

The lithiation reaction of the η -(Cu,Ni)₆Sn₅ anode produced on a Cu-6Ni current collector is subsequently studied by synchrotron PXRD. In agreement with the TEM SAED data (Fig. 7c and 7d, synchrotron PXRD confirms that the anode has the high temperature η -Cu₆Sn₅ polymorph crystal structure. The PXRD patterns in Fig. 8 show the fresh anode grown between a Cu-6Ni/Sn couple contains only hexagonal η -(Cu,Ni)₆Sn₅ and FCC Cu-6Ni. The intensities of the (Cu,Ni)₆Sn₅ peaks gradually reduce as the anode is lithiated to lower potentials, while the broad peaks associated with the lithiated compounds, Li₁₃Cu₆Sn₅ and Li_(13+y)Sn₅, intensify. The anode material is fully reacted with Li-ion when it is lithiated to 0.02 V, and the (Cu,Ni)₆Sn₅ peaks have fully disappeared.

The PXRD pattern of the fully delithiated anode after 1 cycle is dominated by the (Cu,Ni)₆Sn₅ peaks, demonstrating the reversibility of the anode. The full width at half maximum (FWHM) of the (Cu,Ni)₆Sn₅ peaks in the cycled anode are broader than those from the fresh anode, implying that the grain sizes have reduced upon the lithiation/delithiation process[3]. The average grain size for the fresh and 1 cycle sample analysed by Rietveld refinement are 482 nm and 117 nm respectively (details in Table F.1, Supplementary material). The refinement results show good fits between the data and model with R_{wp} s below 10. The average grain size of the fresh electrode is an order of magnitude smaller than those fabricated on a pure Cu current collector (482 nm vs. 9.8 μ m [3]), while upon completing the

first cycle, the grain size reduction is less pronounced in the $(\text{Cu,Ni})_6\text{Sn}_5$ electrode in comparison to the Cu_6Sn_5 electrode (117nm vs. 51 nm [3]). Overall, the PXRD patterns compliment the electrochemical data, suggesting that the lithiation reactions of the η - $(\text{Cu,Ni})_6\text{Sn}_5$ are similar to η' - Cu_6Sn_5 discussed in detail elsewhere [3]. Further detailed characterisation of the electrochemical performance of this anode material will be the focus of future work.

Fig. 8. Synchrotron PXRD patterns of the $(\text{Cu,Ni})_6\text{Sn}_5$ anode at different charge states.

4 Conclusion. Rapid fabrication of $(\text{Cu,Ni})_6\text{Sn}_5$ anodes for LIB applications is realised via the alloying of Ni to the Cu current collector. The resultant anode is free of Cu_3Sn and has the preferred high temperature η - Cu_6Sn_5 structure with open channels which facilitate lithium transportation. The accelerated growth of $(\text{Cu,Ni})_6\text{Sn}_5$ is a result of:

- i. Shorter diffusion pathways due to spalling of IMCs in the porous layer.
- ii. Faster diffusion rates due to a) smaller grains and b) the assumed weaker GBs in the dense IMC layer due to the formation of grains with heterogeneous compositions; and

- iii. Faster nucleation due to a) the reduced solubility of Cu in the melt with increasing amounts of Ni [9] and b) the lower diffusion rate of Ni compared to Cu, resulting in high Ni and Cu concentrations in the melt close to the interface;

This rapid growth can significantly reduce the processing time for anode manufacture enabling a continuous production process with existing equipment and technologies in the soldering industry. The electrochemical functionality of the electrode is validated, and detailed characterisation of electrochemical performances will be performed in future work.

In Vuorinen et al's work [9], the reported optimum Ni content for the fastest IMCs growth is around 9.3 wt% Ni (10 at% Ni). The IMCs growth rate reduces dramatically when the Ni concentration is reduced, while the thickness reduction with increasing Ni concentration from this optima is more gradual. Drawing from the insights gained in this study, it is hypothesized that the optimum Ni content is reached when the segregation of Ni results in the weakest GBs, which in turn lead to increased spalling, smaller grains, and faster GB diffusion. As discussed, with increasing Ni content, the solubility of Cu in the melt will continue to reduce and the concentration of (Ni + Cu) close to the interface will continue to increase due to the slower diffusion rate of Ni, both promoting the formation of IMCs. These competing factors are likely the reasons for the slower decrease in IMCs growth rate at Ni contents above the optima.

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Data Availability. The authors declare that the data supporting the findings of this study are available within the paper and its supplementary material.

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Graphical abstract

In-situ synchrotron X-ray radiography

IMC spalling

CRedit author statement

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Rapid fabrication of $(\text{Cu,Ni})_6\text{Sn}_5$ anodes is achieved on Cu-xNi current collectors.
- The fabrication process dynamics is studied by in-situ synchrotron X-ray imaging.
- EBSD and TEM reveal Ni induces smaller grain sizes and weaker grain boundaries.
- Fast diffusion is a result of shorter diffusion path and increased boundary diffusion.
- Synchrotron powder XRD shows a reversible lithiation/delithiation reaction.