Lithium Diffusion in Copper:

Supporting Information

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Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

Depth profiles of the lithium concentration were measured with an ionTOF TOF.SIMS 5 spectrometer, using a 1 keV Cs^+ beam (50 nA current) for sputtering and a 30 keV Bi_5^+ analysing beam (0.11 pA current). The measured area was 200 µm x 200 µm. After the depth profile was recorded, the depth of the sputter crater was measured with a Bruker DektakXT stylus profilometer to convert the measured fluence to depth. Conversion of the intensity into concentration was done by first determining the Relative Sensitivity Factor (RSF) of Li in Cu with two methods:

1. For the indiffusion experiments, the RSF was calculated by creating a Cu-Li standard with a known concentration. The procedure to make the standard alloy was adapted from Mendelsohn *et al.*[1]. A Cu crucible and lid with a combined mass of 20.0 g were fabricated from OFHC Cu (99.95+ %; Goodfellow) and etched in 5 % sulfuric acid. Lithium with a mass of 0.2 g was added into the Cu crucible within an Ar-filled glovebox. It was then set into a BN crucible, which was afterwards sealed with Parafilm to avoid exposure of the lithium to air. The subsequent heat treatment (Table S1) was done under a flow of 3 sccm of 5 % H_2/Ar in a tube furnace.

Table S1. Heat treatment process for the alloying of Cu with Li and creation of a Cu-Li standard.

Step	Temperature	Time	Function
1	350 °C	18 h	avoid Li loss
2	1100 °C	20 min	melting
3	800 °C	19 h	homogenization

Rapid cooling between steps was ensured by removing the quartz tube from the hot furnace and cooling it with forced air, without exposing the sample to the atmosphere. This was done for all

steps to avoid segregation of phases, especially when cooling from the liquid state after melting of the Cu crucible. The furnace was always preheated between steps before the tube was added. Composition and temperatures were chosen to decrease the risk of forming the Cu_2Li_3 intermetallic phase or regions of liquid lithium during the heat treatment. A 1 mm thin disk was then machined out of the center of the resulting alloy in horizontal orientation to avoid fluctuations of Li concentration within the sample due to gravitational effects during the melting process. One half of the disk was used to determine the lithium concentration by Inductively Coupled Plasma Atomic Emission Spectroscopy (Thermo Scientific ICAP 6500; ICP-AES), which was found to be 0.95 wt.-% (= 8.70 at.-%). The other half was polished and a Tof-SIMS depth profile was measured until the lithium and copper signals were stable. From the respective values, a RSF of 1.31 x 10^{22} cm^{-3} was calculated.

2. After Li^+-ion implantation the as-implanted depth profile was measured by ToF-SIMS (see Figure 3). By integration of the lithium signal and normalization with the known fluence of 1.47 x 10^{16} cm^{-2}, the RSF was calculated to be 1.38 x 10^{22} cm^{-3}, which is in good agreement with the value that was gained from the Cu-Li standard.

Indiffusion from metallic lithium

Indiffusion in solid phase was done by pressing polished Li-metal onto the respective Cu sample in a spring-loaded stainless steel holder and subsequently annealing it under inert Ar-atmosphere. After being cooled to room temperature, the sample was exposed to air and the Li-metal was removed from the Cu surface, which was ensured by washing in demineralized water. The sample was then transferred to the ToF-SIMS and the concentration depth profile was measured.

For measurement of grain boundary diffusion coefficients, polycrystalline Cu disks (> 99.99 %; rolled; Goodfellow Cambridge Ltd.) with an average grain size of 11.9 ± 2.7 µm were used. The average grain size was determined with the *Heyn Lineal Intercept Procedure* (ASTM

standard E112-12) of optical micrographs after polishing and etching of the grain boundaries. Lithium was allowed to diffuse into the mechanically and electrochemically polished samples for 11 days at temperatures between 30 °C and 120 °C. The lattice diffusion coefficients were extracted from similar experiments, with the exception of using electrochemically polished Cu single crystals (> 99.99 %; <100> ± 2°; MTI corporation) and adapting the annealing times. Electrochemical polishing was done in 85 % H_3PO_4 for 20 minutes at 1.2 V vs. Ag/AgCl. The respective temperatures and annealing times for indiffusion from metallic lithium or from a Li^+-containing electrolyte (PYR13, see next section) into polycrystalline (PX) and single crystalline (SX) Cu samples and are listed in Table S2.

Table S2. Annealing temperatures and times for indiffusion from metallic Li or a Li^+-containing ionic liquid (PYR13) into polycrystalline (PX) or single crystalline (SX) Cu samples.

Sample	Li Source	Temperature	Time
SX(100)	Metal	25 °C	28 days
SX(100)	Metal	70 °C	28 days
SX(100)	Metal	100 °C	28 days
SX(100)	Metal	120 °C	28 days
SX(100)	Metal	140 °C	15 days
SX(100)	Metal	160 °C	8 days
PX	Metal	70 °C	11 days
PX	Metal	120 °C	11 days
PX	PYR13	30 °C	11 days
PX	PYR13	70 °C	11 days

Indiffusion from electrolytes

As mentioned in the main article, indiffusion of lithium into copper is not only possible from metallic lithium, but also from a Li^+-containing electrolyte. Here we used lithium

bis(trifluoromethanesulfonyl)imide: 1-ethyl-1-propylpyrrolidinium bis(fluorosulfonyl)imide (1:9 mol ratio; PYR13; Solvionic). Polycrystalline Cu and Li were pressed together by a spring within a coin-cell case (CR 2032 format, SS-316 material), but separated by a glass microfiber filter (Whatman GF/D) with 300 ml PYR13. Different cells were then short-circuited (no induced Li plating) while being maintained at different temperatures (see Table S2). The ionic liquid is not electrochemically stable at 0 V vs. Li^{+}/Li and a solid electrolyte interphase (SEI) is created on the copper surface. After annealing of the samples, they were removed from the coin-cell in air and washed with demineralized water to remove the SEI, before being transferred to the TOF-SIMS. Complete removal was ensured by TOF-SIMS measurements before and after washing with water. While the SEI can potentially influence the boundary conditions at the copper surface, it does not stop lithium from diffusing into copper and does not influence the resulting diffusion coefficients. The ToF-SIMS depth profiles after indiffusion for 11 days into a Cu polycrystal with an average grain size of 11.9 μm are shown for 25 °C and 70 °C in Figure S1.

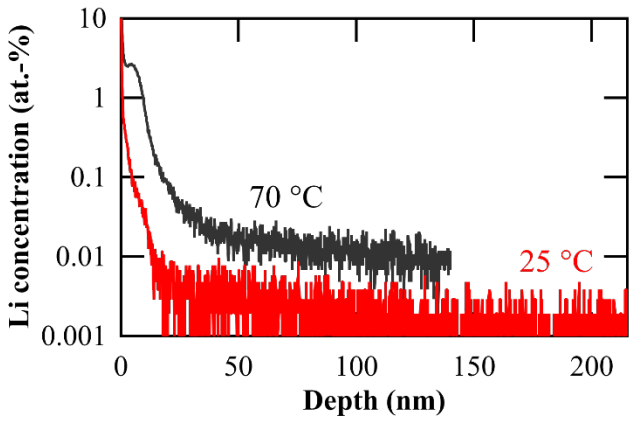

Figure S1. ToF-SIMS depth profile of Li in a Cu polycrystal after indiffusion from PYR13 at 25 °C and 70 °C respectively for 11 days.

Even though no metallic lithium was plated on the copper sample, it is evident that lithium can diffuse into Cu from the ionic liquid. The diffusion is enhanced at higher temperatures and the

extracted diffusion coefficients (in the C-type regime) are in very good agreement with the values extracted from the experiments with indiffusion from metallic Li or from a (see Figure 4).

Ion-implantation and the effect of induced vacancies on peak-broadening

The implantation of Li^+ in Cu single crystals was done with a high current implanter at the Institute for Nuclear and Radiation Physics of the KU Leuven. Li_2SO_4 was used as a Li source with an Ar-plasma for ionization. Mono-energetic Li^+ was implanted with an energy of 60 keV. The substrate normal was thereby tilted by 7° with respect to the ion beam direction to minimize channeling effects and a fluence of 1.47×10^{16} cm^{-2} was chosen to keep the peak concentration under 1 %. After ion-implantation, the samples were transferred in air to the TOF-SIMS.

The effect of induced vacancies due to ion-implantation on lithium diffusion, and therefore on the measured depth profiles, is discussed for the annealed depth profiles in the main article. As evidence for this reasoning, the residual of the respective fit (see Figure 3) is compared with the modeled vacancy density in Figure S2.

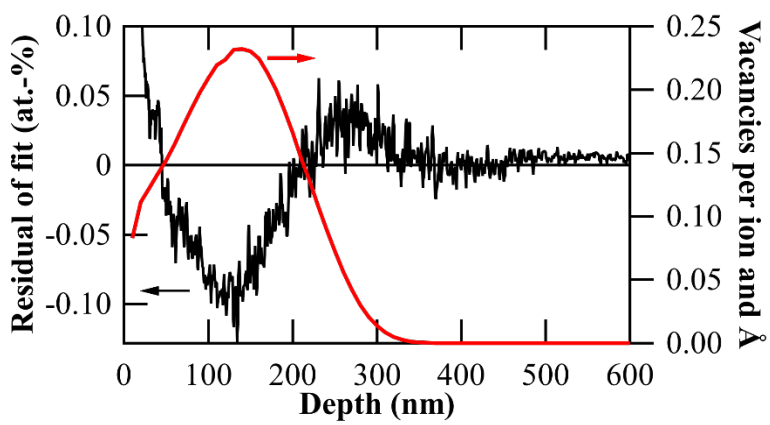

Figure S2. The residual of the fit in Figure 3 is shown in black. The density of produced vacancies was gained from a SRIM model (version SRIM-2013.00 >) for the respective conditions (Li^+-implantation into Cu; 60 keV; 7° tilt) and is displayed in red.

It can be seen in Figure S2 that the maximum deviation between fit and profile of the annealed sample (= residual of fit) coincides in position with the maximum of the induced vacancy

concentration. This is a good indication that the induced vacancies do indeed accelerate lithium diffusion locally and result in fast outdiffusion in this region. The lithium concentration in the neighboring bulk material is consequently increased (positive residual). It should be noted, however, that Figure 3 shows the calculated total amount of generated vacancies during ion-implantation. The actual amount of defects that is present during consecutive annealing at elevated temperatures and that can contribute in increasing the local diffusion coefficient is expected to be much smaller. This is due to recovery that can be caused by mobile defects at room temperature [3,4]. An example is the recombination of interstitials and vacancies just after their creation.

Apart from the introduction of point defects during ion-implantation, also the creation of an amorphous copper layer could be possible. Whether such a layer is created during Li^+-implantation is not yet clear, since its detection requires extensive studies. However, even if an amorphous layer is created, it is not expected to have a noticeable influence on the measured results. Brown *et al*. calculated the glass transition temperature of pure copper to lie at approximately 400 K. Since this temperature is below any annealing temperature that was used for the implantation method, potentially created amorphous copper is expected to crystallize rapidly during sample heating.

References

(1) Mendelsohn, M. H.; Gruen, D. M.; Krauss, A. R. Recent Results on the Preparation and Properties of Li-Containing Cu Alloys. *J. Nucl. Mater.* **1986**, *141–143*, 184–187.

(2) Ziegler, J. F.; Biersack, J. P.; Ziegler, M. D. SRIM - The Stopping and Range of Ions in Matter. 2015.

(3) Echt, O.; Recknagel, E.; Weidinger, A.; Wichert, T. Impurity-Defect Configurations in Ion-Irradiated Copper Studied by the DPAC-Technique with 111In. *Zeitschrift für Phys. B Condens. Matter Quanta* **1978**, *32* (1), 59–66.

(4) Swanson, M. L.; Howe, L. M.; Quenneville, A. F. Investigation of the Interaction between Irradiation-Induced Defects and Solute Atoms in Dilute Copper Alloys by Ion Channeling. *Radiat. Eff.* **1976**, *28*, 205–214.

(5) Brown, T. M.; Adams, J. B. EAM calculations of the thermodynamics of amorphous copper. J. Non-Cryst. Solids **1995**, 180, 275-284.