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Towards lithium-free solid-state batteries with nanoscale Ag/Cu sputtered bilayer electrodes†

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Enhancing the reversible Li growth efficiency in "Li-free" solid-state batteries is key for the deployment of this technology. Here, we demonstrate a nanoscale material design path that enables the reversible cycling of a lithium-free solid-state battery, using $Li_7La_3Zr_2O_{12}$ (LLZO) electrolyte. By means of nanometric Ag–Cu bilayers, directly sputtered onto the LLZO, we can effectively control Li deposition. The robust thin film bilayer, which is compatible with LLZO, enables stable cycling, accommodating the volume changes without the need for extra external pressure.

Solid-state batteries (SSBs) show great promise in facilitating the widespread adoption of electric vehicles.[1,2] Along with the replacement of flammable liquid electrolytes, which would lead to higher safety standards, SSBs may enable the use of lithium metal as anode, allowing for a dramatic increase in energy density, especially compared to standard graphite anodes.[3] However, due to the high Li-reactivity, the assembly of pure Li–metal with solid-electrolytes (SEs) with a low SE-Li interfacial resistance remains a major challenge from both manufacturing and processing points of view.[4]

In this regard, the "Li-free" cell concept, in which the Li metal anode is *in situ* electroplated onto the current collector (CC), represents an opportunity to circumvent the aforesaid challenges.[5,6] Moreover, it allows for minimizing the amount of required lithium, resulting in cost and sustainability improvements. In this context, LLZO is an appealing electrolyte to develop such a battery architecture, due to its high ionic conductivity and excellent stability against Li metal.[7] In

addition, unlike thin-film batteries,[6] limited to tens of $\mu A\ cm^{-2}$, bulk LLZO enables high-power and energy applications. However, recent studies investigating the Li nucleation behaviour at the SE/CC report that Li is plated with a non-uniform morphology, resulting in highly heterogeneous interfaces.[8,9] This would inhibit the growth of lithium as a film-like anode, leading to unexpectedly premature short circuiting.[8–10] Intriguingly, the lithium-growth characteristics can be significantly improved when the SE surface is modified by an artificial interlayer, such as AgC,[11] Ag,[12–14] or Au.[15–17] These materials alloy with lithium at a potential that is very close to that of the Li/Li^+ redox reaction, thus suppressing the nucleation barriers.[15,18] This is in contrast to the case of Si or Sn,[19,20] which undergo major structural changes while alloying with lithium. As a result, the lithium deposition at the CC can potentially be effectively regulated, with the Ag or Au interlayer acting, during battery operation, as a sort of dynamic buffer layer for homogenous lithium redistribution.[15,18]

Herein, we focus on the development of optimal artificial interfaces by sputtering a nanometric bilayer on top of an LLZO-SE, consisting of a 100 nm thick Ag dynamic buffer interlayer, and of a Cu layer, either 600 nm or 900 nm thick, which acts as a CC. Cu has been selected as the CC because of its high electrical conductivity and electro(chemical) stability against both Ag and Li.[21,22] Directly sputtering onto the LLZO-SE is key to minimize the interfacial resistance that would ordinarily be unreachable for current collector foils. A schematic representation of the "Li-free" solid-state half-cell configuration, including its specific layer sequence and thicknesses, is shown in Fig. 1(a). The sputter deposition of Ag and Cu has been carried out at room temperature using a pressure of 4×10^{-1} Pa of pure Ar atmosphere without breaking the vacuum (base pressure lower than 1.2×10^{-5} Pa), to ensure high quality LLZO/Ag and Ag/Cu interfaces. Fig. 1(b) depicts the fabrication steps of the nanometric bilayer.

To investigate the formation of the Li–Ag alloy, we first assembled a Li/LLZO/Ag(100 nm)/Cu-foil half-cell. The Cu-foil was used to facilitate the post-mortem analysis by peeling it after the Li deposition. Fig. 2(a) shows the electrochemical

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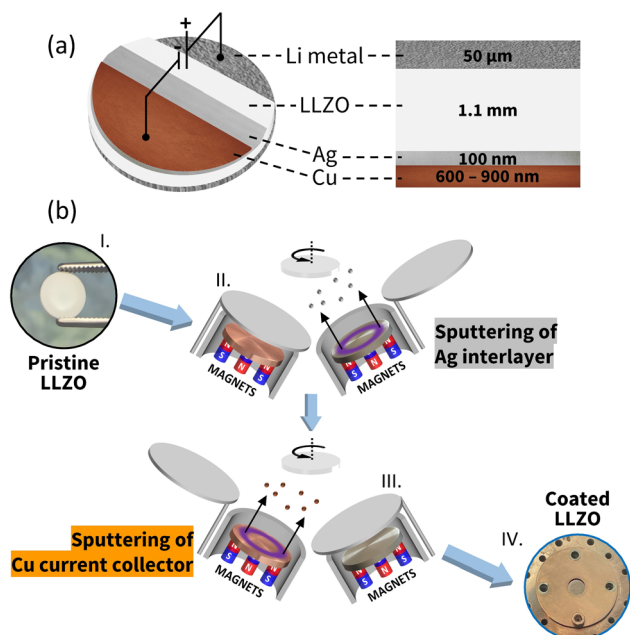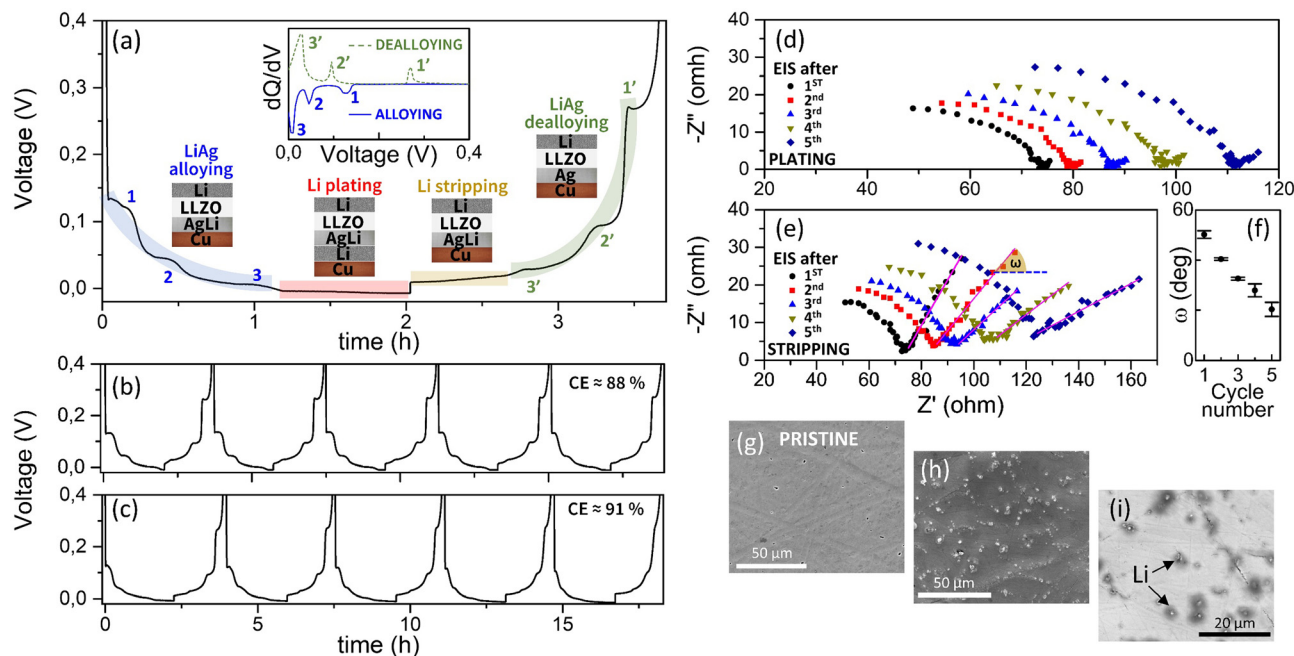† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3cc02942e

Fig. 3 (a) Initial potential response of Li/LLZO/Ag(100 nm)/Cu(600 nm) after plating/stripping at j = 0.05 mA cm^{-2} and at T = 70 °C. The schematics show the layer structure evolution upon cycling; the inset shows the differential capacity as a function of the cell voltage. Voltage profile of (b) Li/LLZO/Ag(100 nm)/Cu(900 nm) and (c) Li/LLZO/Ag(100 nm)/Cu(600 nm) at j = 0.05 mA cm^{-2} and at T = 70 °C. Impedance spectra of Li/LLZO/Ag(100 nm)/Cu(600 nm) after plating (d) and stripping (e) steps at a current density j = 0.05 mA cm^{-2} at T = 70 °C. (f) Warburg angle ω as a function of cycle number. (g) SEM images of the Cu surface before any electrochemical testing. *Ex situ* SEM (h) and BSE (i) of the Cu surface after 5 plating/stripping cycles at j = 0.05 mA cm^{-2} plus 5 plating/stripping cycles at j = 0.10 mA cm^{-2}.

The reversibility of the Li plating through the Ag$_x$Li$_y$ layer onto a thin sputtered Cu CC was investigated by continuous plating/stripping processes. Fig. 3(a) shows the whole cycling profile of the Li/LLZO/Ag(100 nm)/Cu(600 nm) cell. Three "discharge" voltage steps are clearly distinguishable at $V \approx$ 7 mV, 45 mV, and 120 mV, highlighted in (light) blue, followed by the Li plating at $V <$ 0 V. By taking into account the theoretical conversion of a 1 mA h cm^{-2} to 5 μm thick Li layer,[30] as explained in detail in the supplementary materials, the evolution of the corresponding alloy stoichiometries (and errors) may also be calculated. This would lead to the alloying sequence of Ag → (1) Ag$_{86\pm2}$Li$_{14\pm2}$ → (2) Ag$_{58\pm6}$Li$_{42\pm6}$ → (3) Ag$_{37\pm6}$Li$_{63\pm6}$, with the latest value being different with respect to the one calculated by the XRD peak position. However, due to the inherent error of the Li quantity conversion that assumes a perfect process, which may not occur in the reality, such values could overestimate the Li quantity in the alloys and be less accurate than the ones extracted from the X-ray measurements.

Besides, the reversibility of the process is confirmed by the similar plateaus observed at $V \approx$ 27 mV, 95 mV, and 270 mV, highlighted in light green, corresponding to the dealloying reaction sequence. In between, the plateaux related to the plating and stripping of Li onto the Cu CC are visible and highlighted in red (plating) and yellow (stripping). The inset in Fig. 3(a) displays the differential capacity as a function of the cell voltage, for the alloying process in (blue) solid line and for the dealloying process in (green) short dashed line. Three well

defined peaks for each galvanostatic process are visible, named 1 (1'), 2 (2'), and 3 (3'). Their positions along the x-axis, related to the same process, exhibit different voltage shifts, which indicates a stronger cell polarization for the Ag → (1) Ag$_{86\pm2}$Li$_{14\pm2}$ reaction. This suggests that, by having an Ag$_x$Li$_y$ alloy as the starting interlayer, the cell polarization may be fairly reduced, since the Ag-rich (de-)alloying processes would be avoided, as long as the corresponding reaction voltage would not be accessed while cycling.[13]

The full cycling of the half-cells with Cu (900 nm) and Cu (600 nm), upon applying the same cycling parameters as in Fig. 3(a) are displayed in Fig. 3(b) and (c), respectively. In both cases, the voltage profile is similar upon increasing the number of plating/stripping processes irrespective of the Cu thickness. This would further demonstrate that the three plating/stripping steps are ascribable to the Ag–Li (de-)alloy formation. The promising Coulombic efficiency (CE), obtained from the full process (alloying and plating) and averaged over the first 5 cycles, is above 88% for both cells, confirming the viability of our nanoscale anode material design pathway. The slight differences in the voltage profile and CE are likely due to the differences in the surface roughness and ionic conductivity from pellet to pellet.[7] However, here, the CE does not pretend to point to a battery performance improvement, for which a far longer cycle performance study would be needed.

Galvanostatic electrochemical impedance spectroscopy (GEIS) was carried out to gain further insight into the evolution of the interfacial resistance and the Ag interlayer during the

consecutive plating/stripping processes. The corresponding Nyquist plots are shown in Fig. 3(d), after each plating step, and in Fig. 3(e), after the subsequent stripping processes. The spectra in Fig. 3(d) are characterized by a semicircle at high frequency, ascribed to the interfacial resistance between the Li electrode and the LLZO electrolyte, which is partially measured due to the frequency range selected for this experiment (10 kHz to 1 Hz). This resistance seems to slightly increase at each plating step. More importantly, at low frequencies, the capacitive behaviour of the blocking CC to Li$^+$ is barely visible, since, after Ag$_x$Li$_y$ alloy formation, and after Li deposition onto the Cu, the anodic part of the cell converts into a charge transfer component, due to the non-blocking nature of Li. On the contrary, after each stripping step, the impedance spectra exhibit solely capacitive behaviour at low frequencies due to the recovered blocking nature of the CC, suggesting the potential complete de-alloying process of Ag$_x$Li$_y$. The characteristic Warburg diffusion element, represented by the tail appearing at low frequency, should show a phase angle $\omega = 45°$. However, as shown in Fig. 3(f), ω decreases upon increasing the number of plating/stripping cycles, which may indicate a chemical or structural evolution of the Ag/Cu bilayer upon alloying/dealloying consecutive processes. Moreover, an increase in resistance is also visible, as in the plating case, which can be due to the contact loss at the LLZO/Ag interface.

SEM micrographs performed after GEIS are reported in Fig. 3(h) and (i), together with the pristine sample in Fig. 3(g). The SEM micrographs reveal that the addition of the Ag layer prevents the Cu-CC from breaking during stripping/plating.[8,17,31] In fact, due to alloying of Li and Ag, nucleation of Li onto Cu may then be more homogeneous because the AgLi layer acts as a seed layer for Li nucleation.

In this study, we have investigated the effect of Ag–Cu bilayer nanomaterials on the electrochemical lithium deposition. We found that the lithium nucleation and growth behaviour is significantly altered by the LLZO surface modification thanks to the artificial interlayer, and that lithium distribution on the Cu-CC can be effectively controlled. Considering the convenience of interlayer sputter deposition on the LLZO surface and its wide applicability, we expect that our findings will provide useful guidelines for designing optimal interfaces for solid state batteries, especially enabling a "Li-free" sample architecture. Moreover, this work poses the basis for more applied and consecutive ones, that might focus on long cycle performance of the half and full cell. Finally, given the generality of the Li–Ag alloy formation, we expect that our findings will extend to many different garnet electrolyte materials and metallic current collectors.

Conflicts of interest

There are no conflicts to declare.

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