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Editorial

Phase-dependent lithium-alloying reactions for lithium-metal batteries

With the increasing demand for higher energy lithium-ion batteries (LIBs), it is imperative to develop high-capacity electrode materials [1–4]. Due to the unique electrochemical Li-alloying reactions, Li-alloys offer high theoretical capacity, especially lithium-rich phase alloys, which exceeds the theoretical capacity of graphite anodes [5–7]. Phase-transition, which significantly influences lithium alloy reactions, determines high voltage hysteresis, low Coulombic efficiency (CE), and short cycling life [8,9]. However, the role of intermetallic compounds and solid-solutions phases in the Li-alloying process still remains controversial.

Recently, Ji's group investigated three representative Li-alloys: Li-Ag alloy with Li-rich solid-solutions region, Li-Zn alloy with solid-solutions phase, and Li-Al alloy with intermetallic compound phase [10]. The solid-solutions phase can realize superior reversibility of Li-alloying/dealloying, since it has lower phase-transition energy barrier than the intermetallic compounds due to subtle structural changes and chemical potential gradients established within the solid-solutions. As shown in Fig. 1a, depth profiling analysis of the electrode was performed by *ex-situ* time of flight secondary ion mass spectrometry (TOF-SIMS). For the cycled $Li_{20}Ag$ alloy, the Ag^-/Li^- intensity ratio remained constant during ion sputtering, which suggested uniform distribution of Li and Ag along the vertical direction of the foil. For $Li_{20}Zn$, Zn was mainly enriched in the top and bottom layers of the alloy foil. For $Li_{20}Al$, Al preferentially accumulated on the upper surface of $Li_{20}Al$.

The diffusion mechanisms of lithium and delithiation in the Li-alloy phase was given in Figs. 1b and c. For solid-solution alloys, the continuous chemical potential gradient drives uniform diffusion of M (M = Ag, Zn, Al) and Li ions across the bulk phase. Intermetallic compounds with fixed stoichiometry exhibited chemical potential difference at the interfaces between adjacent phases. There is no driving force for elements to diffuse into the bulk phase of the alloy, which leads to higher phase-transition energy barriers. Moreover, the battery constructed by Li-rich $Li_{20}Ag$ alloy anode and a $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode exhibited significant capacity retention rate of 87% after 250 cycles, with a Coulombic efficiency of 99.8% ± 0.1% (Fig. 1d). The work demonstrates that Li-rich $Li_{20}Ag$ alloy hosts potential application.

In summary, Ji's group confirmed subtle structural changes and chemical potential gradients in the solid-solution phase contributed to phase-transition and lithium atom migration during Li-alloying/dealloying processes, and also found the effective method for avoiding the formation of dendrites and suppressing parasitic reactions. The results provide new direction for exploring high-performance alloy electrodes for rechargeable metal batteries.

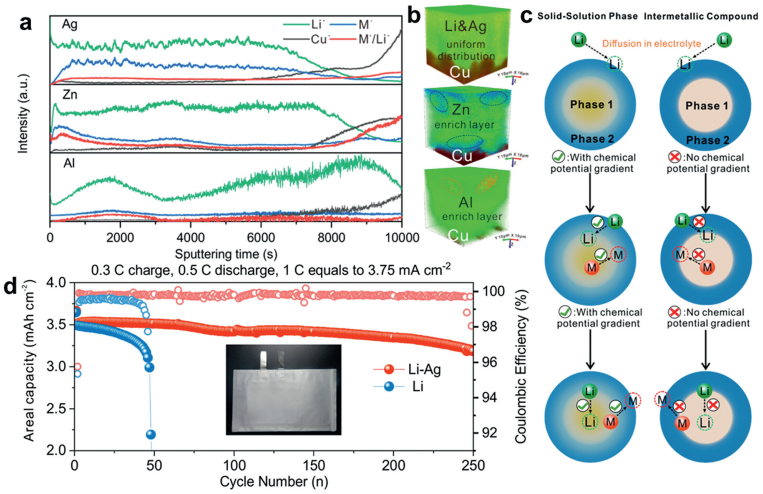

Fig. 1. (a) TOF-SIMS depth profile analysis and (b) corresponding reconstructed 3D images for Li-Ag, Li-Zn and Li-Al alloys. (c) Diffusion mechanisms of solid-solution and intermetallic alloys. (d) Cycling performance of $Li_{20}Ag||NCM811$ pouch cells. Reproduced and adapted with permission [10]. Copyright 2014, American Chemical Society.

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