



## Editorial

## Exploring synthetic strategy for stabilizing nickel-rich layered oxide cathodes through structural design



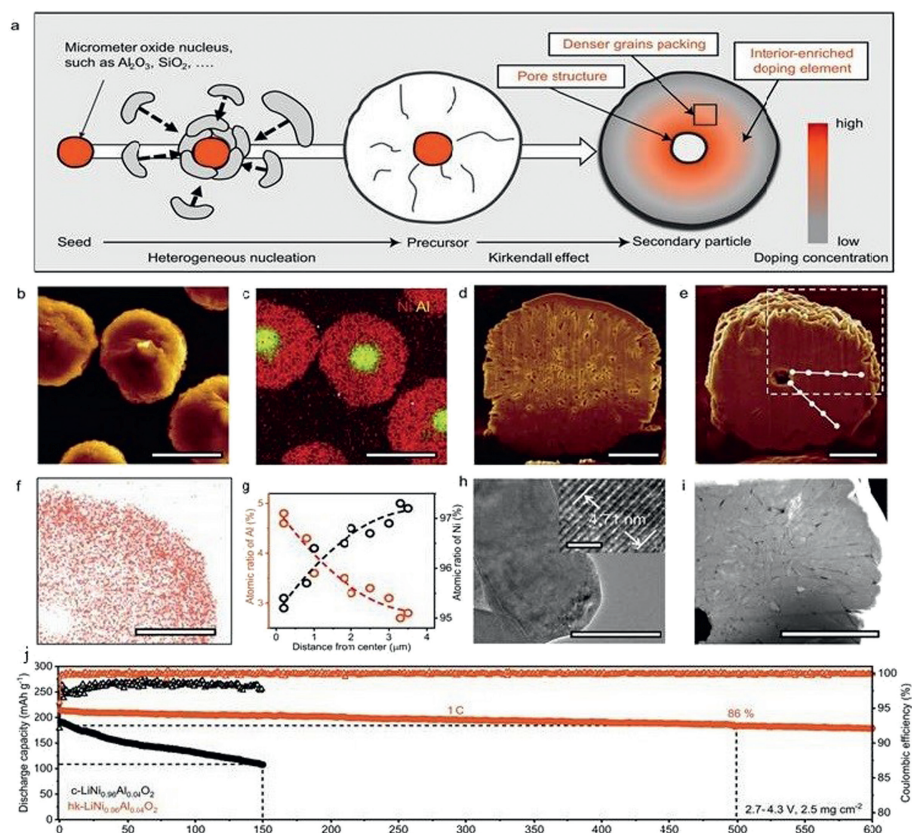
With the increasing demand for battery energy density, there is an urgent need to develop cathode materials with high energy density and long cycling life [1]. Nickel-rich layered oxide (NRLO) materials are expected to become next-generation cathode materials for power batteries due to their high specific capacity and relatively low material cost [2]. However, there are microstructural changes and crack formation for NRLO materials during cycling processes [3]. The existing methods to alleviate structural degradation can delay pulverization [4], but could not adjust stress distribution and suppress crack formation. Thus, it is crucial to develop strategies for uniform stress distribution in stabilizing NRLO particles.

Li's group recently has proposed the combined strategy of heterogeneous nucleation and Kirkendall effect for optimizing the stress-strain state and uniform distribute stress within particles to improve the stability of NRLO materials effectively [5]. As shown in Fig. 1a, heterogeneous nucleation is carried out on the introduced exotic metal/metalloid oxide seeds during the coprecipitation process, followed by solid-state Kirkendall effect during high-temperature annealing process. During the annealing process, the diffusion coefficient of Al atoms is much greater than that of Ni. The annealing process promotes the diffusion of Al atoms towards the outer layer, leading to the formation of voids in the center of secondary particles and the formation of an Al-rich internal doping structure. Through scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) observations (Figs. 1b and c), the core-shell precursor particles are composed of Al element mainly in the core and Ni element mainly in the outer shell. Notably, there are significant differences in the cross-sectional morphology of the material after annealing. The structure of  $\text{c-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$  particles with many small cavities inside prepared by conventional methods is relatively loose (Fig. 1d), which can easily evolve into cracks while there are no obvious small cavities

and only a micro-sized central void for the internal structure of  $\text{hk-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$  is formed (Fig. 1e).

As shown in Figs. 1f and g, the Ni concentration of secondary particles gradually increases from the inside due to the Kirkendall effect while the concentration of Al is decreased from  $\sim 5\%$  in the core region to  $<3\%$  on the particle surface. Al doping can reduce the lattice volume effect during de-lithiation process, as which becomes more obvious with doping content increasing. In addition, the Al rich core can better withstand strain and maintain good mechanical integrity during cycling since cracks mainly form in the core area. As shown in Fig. 1h, the smaller primary particle size of the  $\text{hk-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$  prepared by this method is smaller. In HAADF-STEM image (Fig. 1i), the closely tight  $\text{hk-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$  particles could facilitate the transfer of ions and electrons at the interface, which reduces mechanical crushing and homogenizes the charge distribution inside the secondary particles. The small grains near the Kirkendall void structure can effectively reduce the shrinkage during  $\text{Li}^+$  extraction for uniformizing the stress distribution. The enhanced mechanical stability helps to reduce the irreversible  $\text{Li}^+$  consumption and the dissolution of transition metal (Ni), which can result in excellent long-term electrochemical stability of  $\text{hk-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$ . As expected,  $\text{hk-LiNi}_{0.96}\text{Al}_{0.04}\text{O}_2$  exhibits an 86% capacity retention rate and an average capacity loss of 0.028% per cycle after 500 cycles (Fig. 1j).

In conclusion, Li *et al.* proposed the combined strategy of heterogeneous nucleation and Kirkendall effect for constructing NRLOs with unique morphology and element distribution. The as-synthesized NRLO could effectively alleviate crack formation caused by uneven stress distribution. This work not only provides new guidance for the further development of NRLO materials, but also provides new ideas for improving the performance of secondary particles.



**Fig. 1.** (a) Illustrative heterogeneous nucleation and Kirkendall effect-induced synthesis route. (b, c) Cross-sectional SEM image and EDS mapping of precursor. (d, e) Cross-sectional SEM images of the c-LiNi<sub>0.96</sub>Al<sub>0.04</sub>O<sub>2</sub> and hk-LiNi<sub>0.96</sub>Al<sub>0.04</sub>O<sub>2</sub> secondary particles. (f-h) Composition and morphological characteristics of hk-LiNi<sub>0.96</sub>Al<sub>0.04</sub>O<sub>2</sub> particles. (i) HAADF-STEM image of hk-LiNi<sub>0.96</sub>Al<sub>0.04</sub>O<sub>2</sub> secondary particles. (j) Cycling performance of coin-type cells with graphite anodes at 1C. Scale bar: (b, c) 5 μm; (d–f, i) 2 μm; (h) 100 nm and the scale bar in the inset of (h) is 2 nm. Reproduced with permission [5]. Copyright 2024, Nature Publishing Group.

### Declaration of competing interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

### CRedit authorship contribution statement

**Qiang Wu:** Writing – original draft. **Baofeng Wang:** Writing – review & editing.

Qiang Wu  
Baofeng Wang\*

Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai, 200090, China

\*Corresponding author.

E-mail address: wangbaofeng@shiep.edu.cn (B. Wang).

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