

Surface engineering to prevent oxygen evolution of high-voltage cathodes

A perovskite nanolayer formed at the surface of layered cathode particles enables ultra-stable high-voltage cycling. The lanthanum and calcium-based perovskite layer serves as an oxygen buffer, and effectively suppresses the oxygen evolution reaction that is a common cause of failure in hybrid anion- and cation-redox cathodes.

This is a summary of:

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The problem

Lithium-ion batteries with high discharge energy densities can be achieved by increasing the charging cut-off voltage. Although cathodes such as LiCoO_2 (LCO), Ni-rich, and Li and Mn-rich layered oxides can exhibit extraordinarily high energies at high voltages, a series of problems arise. The equilibrium oxygen partial pressure is dramatically increased at voltages above 4 V, which leads to lattice oxygen release^{1–3}. This oxygen release causes transition-metal migration, irreversible phase transition and electrolyte contamination or exhaustion, decreasing the cycle life of batteries. Surface coatings can be used to mitigate these problems, but they often suffer from poor uniformity and only offer limited improvements in cycling stability. It is vital that cathodes are constructed with high-quality surface architectures that are conformal, do not block Li^+ transport, and also suppress the oxygen evolution reaction (OER)^{4,5}.

The solution

We selected LCO as a model hybrid anion- and cation-redox cathode to test our approach to suppressing the OER. Inspired by the oxygen storage capability of $\text{LaMO}_{3-\delta}$ ($M = \text{Ni, Co, Mn}$) perovskite, we constructed a uniform three-dimensional strained $\text{La}_{1-w}\text{Ca}_w\text{CoO}_{3-\delta}$ nanolayer on the surface of the LCO cathode using a scalable ion-exchange reaction: a process that we refer to as 'lanthanzurization'. This nanolayer enables the ultra-stable cycling of the LCO cathode at 4.6 V, including in pouch-type full cells (Fig. 1a). We extended this strategy to Co-lean Ni-rich and Co-free Li and Mn-rich layered cathodes, and again observed that the treated cathodes have greater stability under high-voltage cycling than the untreated control samples. The reconstructed perovskite nanolayer remains stable even at high voltages and protects the inner layered lattice from degradation. The ion-exchange process is easy to perform and control, which makes it possible to create a thin, uniform, high-quality coating over a large mass of particles.

Detailed structural and spectroscopic characterizations revealed that the high-voltage stability of the treated LCO cathode originates from the reversible oxygen-storage capability and the poor electrocatalytic activity of the surface perovskite layer (Fig. 1b). Specifically, the oxygen produced at high voltages by the oxidized lattice can be stored in the oxygen vacancies of the surface perovskite layer.

This process is highly reversible and the stored oxygen species can later be released and heal the defects in the bulk lattice, thereby suppressing the high-voltage OER. We found that the generation of CO_2 and the formation of unstable cathode–electrolyte interphases are inhibited, owing to the enlarged charge-transfer overpotential of the strained perovskite surface in the electrolyte decomposition reaction. Therefore, harmful side reactions that can occur at high voltages are suppressed, enabling the stable high-voltage operation of the cathodes.

The implications

The aqueous lanthanzurization process enhances the high-voltage cycling stability of layered cathodes and has high scalability and tunability. We showed that this lanthanzurization strategy can also be applied to other cathodes with Co-lean or Co-free chemistries, demonstrating the general applicability of the approach for developing sustainable batteries. The flexibility of our approach is rooted in the vast compositional space of perovskites. Therefore, there are ample opportunities for the future optimization of the nanoscale perovskite coating.

It should be noted that our method has some limitations. First, the ion-exchange reaction takes a long time (more than an hour), which might trigger undesirable side reactions, especially for cathodes sensitive to protonic solvents. Second, only dopants with small ionic radii can be used owing to the limited lattice tolerance; thus, large cations such as Sr^{2+} are difficult to incorporate, which restricts the choice of elements for the A-site of the perovskite. Lastly, the cost of using rare-earth elements, although only in a nanolayer, might restrict the use of this approach for some practical applications, and alternatives using more earth-abundant elements should be sought.

Our study provides new opportunities to directly engineer the atomic architecture on the surface of a cathode, which can be used to increase the performance of cathodes in addition to (bulk and surface) doping and coating approaches. We plan to perform further studies with other energy materials, such as Na-ion cathodes. Moreover, the highly regulated surface properties offer new pathways for the development of solid-state devices, such as high-voltage solid-state batteries.

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EXPERT OPINION

“The authors have developed a new engineering process that is quite distinct from conventional surface doping and coating methods to effectively passivate highly reactive surface oxygen activity in lithium-layered cathode materials for high-voltage operation. I believe that the results

of this study will be useful for researchers in the field of batteries and enrich the cathode engineering pool or toolbox available for achieving high-voltage operation.” **Kisuk Kang, Seoul National University, Seoul, Republic of Korea.**

FIGURE

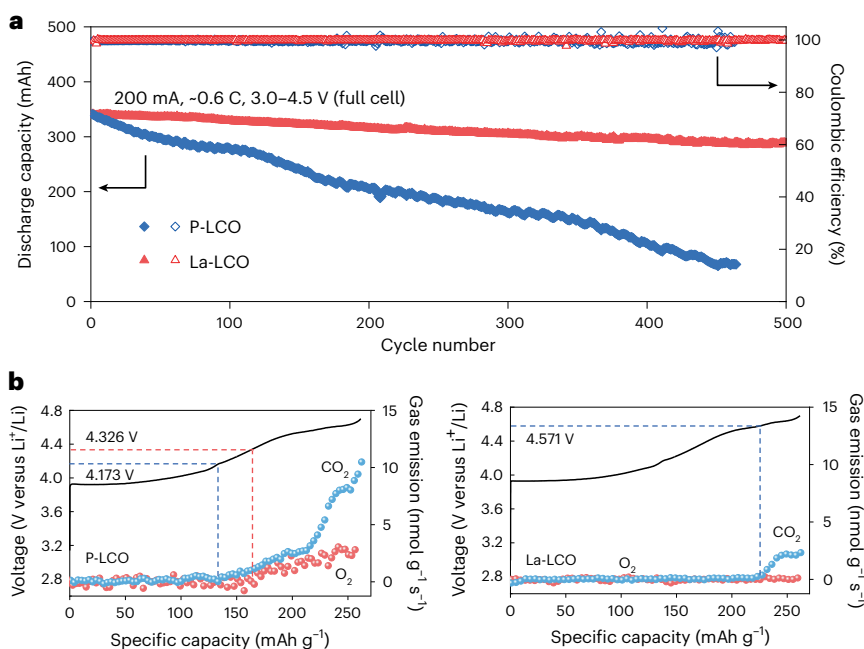


Fig. 1 | Reversible oxygen storage in a reconstructed perovskite surface layer enables stable high-voltage cycling of layered cathodes. **a**, Cycling performance of La-LCO and pristine-LCO (P-LCO) in pouch-type full cells at 3.0–4.5 V. The La-LCO sample maintains its capacity longer than the control P-LCO sample. **b**, Charge curves and in situ differential electrochemical mass spectrometry profiles during the first charge of P-LCO (left) and La-LCO (right). The onset of the release of O₂ (red) and CO₂ (blue) is much delayed for La-LCO compared with the P-LCO control. © 2023, Cai, M. et al.

BEHIND THE PAPER

Initially, we did not expect to obtain a reconstructed perovskite surface layer, and only tried to dope the surface lattice with ions of large radius and high valence to stabilize the labile surface lattice oxygen. After much trial and error, we found that both lanthanum and calcium doping can increase the high-voltage cycling stability. Only then did we begin to study the synergistic effect of the two elements. When developing the process, we spent most of

the time scaling up and extending the wet chemical approach to Ni-rich and Li-rich materials. It was challenging to optimize the process for large-scale synthesis and to overcome the sensitivity of non-LCO cathode materials to water. However, we finally succeeded in demonstrating the scalability and universality of this approach. We are continuing to explore new ways to adapt this strategy. **F.H. & J.L.**

REFERENCES

1. Yan, P. et al. Injection of oxygen vacancies in the bulk lattice of layered cathodes. *Nat. Nanotechnol.* **14**, 602–608 (2019). **This paper reports lattice cavitation and bulk phase transformation from a layered to cation-densified spinel phase in cycled Li-rich layered cathodes.**
2. Dong, Y. & Li, J. Oxide cathodes: Functions, instabilities, self healing, and degradation mitigations. *Chem. Rev.* <https://doi.org/10.1021/acs.chemrev.2c00251> (2022). **An overview of cathode functioning, degradations, and mitigation strategies.**
3. Zhang, J. et al. Trace doping of multiple elements enables stable battery cycling of LiCoO₂ at 4.6 V. *Nat. Energy* **4**, 594–603 (2019). **This paper reports a bulk trace doping method to enable stable cycling of LiCoO₂ at 4.6 V and reveals the synergistic effect of the dopants.**
4. Xu, G. et al. Building ultraconformal protective layers on both secondary and primary particles of layered lithium transition metal oxide cathodes. *Nat. Energy* **4**, 484–494 (2019). **This paper reports a method to build a uniform conductive polymer surface layer at both secondary and primary particle levels of Ni-rich layered cathodes.**
5. Yoon, M. et al. Reactive boride infusion stabilizes Ni-rich cathodes for lithium-ion batteries. *Nat. Energy* **6**, 362–371 (2021). **This study constructs a uniform boride surface coating and grain boundary infusion to stabilize the electrochemical cycling of Ni-rich layered cathodes.**

FROM THE EDITOR

“This work is eye-catching as it presents a highly effective surface engineering approach — that differs from the conventional coating method — to combat the oxygen instability issue that has been plaguing the application of high-voltage layered oxide cathodes. It also analyses cathode degradation mechanisms and proposes design criteria for surface coating.” **Alex Zhang, Senior Editor, Nature Energy.**