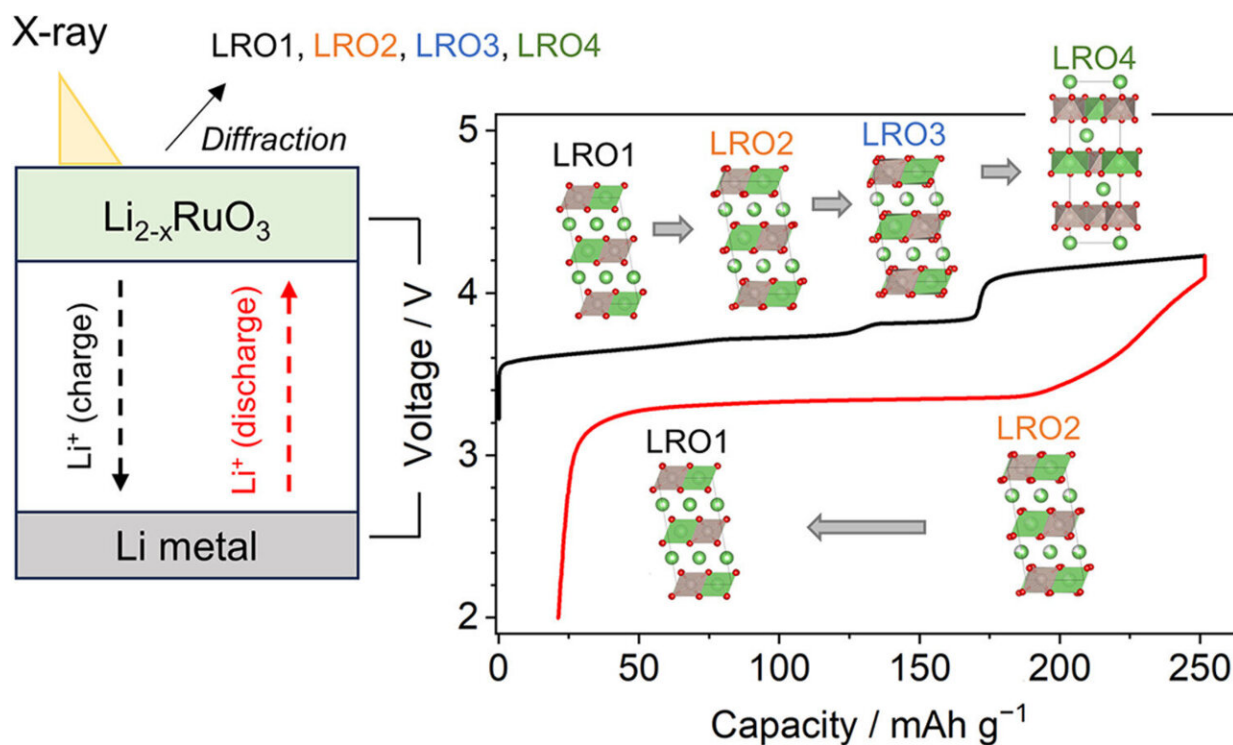


# Hidden cause of lithium-rich cathode materials' low energy efficiency revealed

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Credit: *Energy Storage Materials* (2023). DOI: 10.1016/j.ensm.2023.103051

A research team consisting of the National Institute for Materials Science (NIMS) and SoftBank Corp. has found that voltage hysteresis in  $\text{Li}_2\text{RuO}_3$ —a high-energy-density rechargeable battery cathode material—is caused by differences in the intermediate crystalline phases formed during charge and discharge processes. The study is [published](#) in

## *Energy Storage Materials.*

Voltage hysteresis is a phenomenon detrimental to lithium (Li)-[ion batteries](#) in which [discharge voltage](#) becomes significantly lower than charge voltage. These results revealed a voltage-hysteresis-causing mechanism inconsistent with conventional theory.

Li-rich electrode materials are capable of storing larger amounts of Li ions than conventional Li-ion battery cathode materials (e.g.,  $\text{LiCoO}_2$ ), and Li ions can be stably extracted from and inserted into them. In addition, the energy capacity of these materials ( $> 300 \text{ mAh/g}$ ) is approximately twice that of conventional cathode materials.

Because of these desirable characteristics, Li-rich electrode materials have been researched as viable candidates for next-generation, high-energy-density Li-ion battery cathode materials. They also have a disadvantage, however: Poor charge/discharge energy efficiency due to large voltage hysteresis occurring during charge and discharge.

It has been widely accepted by the [scientific community](#) that voltage hysteresis in Li-rich electrode materials results from irreversible changes in their [crystalline structures](#) during charge and discharge. This research team focused on  $\text{Li}_2\text{RuO}_3$  as a model Li-rich electrode material and closely observed changes in its [crystalline structure](#) while it was being charged and discharged.

Its crystalline structure was found to change reversibly, not irreversibly—it recovered its initial pre-charge crystalline structure by the end of the subsequent discharge. During this charge/discharge cycle, voltage hysteresis was observed in  $\text{Li}_2\text{RuO}_3$  despite the absence of irreversible crystalline structure changes—a result contrary to conventional theory.

The team then closely analyzed crystalline structure changes in an  $\text{Li}_2\text{RuO}_3$  electrode while it was being charged and discharged using various advanced analytical instruments. These analyses revealed a discrepancy in the intermediate crystal phase formed during the charge and discharge processes causing the voltage hysteresis. In other words, voltage hysteresis within a Li-rich electrode material appears to be attributed to different reaction pathways rather than irreversible crystalline structure changes.

Based on these results, the research team plans to evaluate Li-rich electrode materials while focusing on chemical reaction pathways during charge and discharge cycles in addition to measuring voltage hysteresis. This approach is expected to expedite the development of Li-rich electrode materials that will satisfy both high capacity and high charge/discharge energy efficiency requirements.

**More information:** Marcela Calpa et al, Voltage hysteresis hidden in an asymmetric reaction pathway, *Energy Storage Materials* (2023). [DOI: 10.1016/j.ensm.2023.103051](https://doi.org/10.1016/j.ensm.2023.103051)

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