

## BATTERIES

## Fixing faults

“the progressive ordering upon charging ... significantly enlarges the reversible operational range of oxide electrodes”

Layered transition metal oxides with an excess of Na<sup>+</sup> or Li<sup>+</sup> have high theoretical capacities and are thus promising cathode materials for high-energy-density batteries. However, layered transition metal oxides typically undergo irreversible structural degradation upon charging, placing a limit on the achievable capacity. Now, writing in *Nature Communications*, Atsuo Yamada and co-workers show that a Na-rich layered transition metal oxide self-repairs stacking faults upon charging, preventing structural degradation and enabling highly reversible cathode reactions.

Li-ion and Na-ion batteries generally use a layered transition metal oxide, AMO<sub>2</sub> (where A is Li or Na, and M is a transition metal), as the cathode material. Upon charging, A<sup>+</sup> ions are expelled from between the MO<sub>2</sub> layers, and this de-intercalation changes the composition of the material. For the initial compositional

changes of A<sub>x</sub>MO<sub>2</sub> (0.4 < x < 1.0), the corresponding structural changes are reversible; however, the effects of larger compositional changes (0.0 < x < 0.4) upon continued charging are generally irreversible. “Structural degradations such as layer exfoliation and cracks commonly occur upon deep charge and are a major obstacle to achieving high-energy-density batteries,” explains Yamada. Thus, materials with higher theoretical capacities, such as Li-rich or Na-rich layered transition metal oxides (A<sub>2</sub>MO<sub>3</sub>), are currently being explored. Of particular interest to Yamada and colleagues is Na<sub>2</sub>RuO<sub>3</sub>, a model cathode material that does not undergo irreversible degradation even after extraction of a large amount of Na.

The O3 polymorph of Na<sub>2</sub>RuO<sub>3</sub> comprises layers of [Na<sub>1/3</sub>Ru<sub>2/3</sub>]O<sub>2</sub>, in which the cations adopt a honeycomb-like arrangement, with additional Na<sup>+</sup> ions residing between the layers. Using X-ray diffraction, the team reveal that within pristine O3-Na<sub>2</sub>RuO<sub>3</sub>, ~40% of the layers stack incorrectly. In situ X-ray diffraction also enables the structural changes upon charging–discharging to be monitored. Upon charging, the de-intercalation of Na<sup>+</sup> triggers a sequential phase transformation that is accompanied by a substantial decrease in the number of stacking faults. Notably, this self-reorganization of the stacking faults is reversible — the faults re-form upon discharge.

The authors attribute the self-repair of the stacking faults to

cooperative Coulombic interactions. Upon charging, the [Na<sub>1/3</sub>Ru<sub>2/3</sub>]O<sub>2</sub> layers supply Na<sup>+</sup> to the interlayer region to replace Na<sup>+</sup> ions lost through de-intercalation. Subsequent gliding of the layers minimizes repulsive interactions between interlayer Na<sup>+</sup> and Ru<sup>5+</sup> and maximizes attractive interactions between interlayer Na<sup>+</sup> and Na<sup>+</sup> vacancies in the [Na<sub>1/3</sub>Ru<sub>2/3</sub>]O<sub>2</sub> layers. The combined effect energetically favours the formation of a more ordered stacking structure upon charging and, in contrast to AMO<sub>2</sub> materials, prevents irreversible structural degradation for large changes in the composition. “Although counterintuitive, the progressive ordering upon charging could be a general phenomenon for A<sub>2</sub>MO<sub>3</sub> materials and significantly enlarges the reversible operational range of oxide electrodes,” says Yamada.

Although Na<sub>2</sub>RuO<sub>3</sub> shows good operational stability, the cost of the material is prohibitive for practical applications. Nevertheless, the demonstration of ordering upon charging highlights the importance of materials design in manipulating the Coulombic interactions — an approach that could be used to engineer highly reversible electrodes. Indeed, Yamada and his team are looking for ways to control stacking faults and vacancies to enable the phenomenon of ordering upon charging to be extended to other materials comprising more abundant transition metals as well as Li analogues.

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