

it can hybridize, nor does it hybridize with the lithium 2s orbital because of their large energy difference. Its energy level is higher than that found in the classical Li–O–M configuration, which is stabilized by the O–M hybridization, and lower than the antibonding states. These electronic properties mean that, when lithium deintercalates, on charge, the electron from the oxygen anion belonging to the Li–O–Li configuration can be easily removed. The position of the non-bonding t_{2g} orbital in comparison to the energy level of the oxygen 2p orbital depends on the identity of M. Therefore, depending on the nature of M there is a competition between transition-metal oxidation and oxygen oxidation.

Another interesting insight from the work of Ceder and co-workers concerns the formation of O–O pairs. Such peroxo pairs were experimentally observed in ruthenates¹¹, however, they do not appear in Li(Li,Mn,Ni,Co)O₂ phases. This behaviour was also well explained by the calculated electronic structure of these materials. The formation of O–O pairs with a very short distance between the atoms requires the rotation of two neighbouring oxygen atoms

around the central metal atom. However, transition metals with partially filled d-shells, like those in Li(Li,Mn,Ni,Co)O₂ materials, create strong directional bonds that prevent the rotation of the neighbouring oxygen needed to form peroxo species. In good agreement with experimental results, the formation of peroxo species is expected for systems that contain elements with completely filled (or no) d shells (for example, Sn and Sb).

Taken together, these *ab initio* results offer a greater understanding of previously reported data and the work of Bruce and co-workers³; specifically the oxygen oxidation on the high voltage plateau, and the absence of peroxo species due to the presence of transition metals with unfilled d shells. The role played by the Li⁺ ions in the transition-metal layer, demonstrated by the calculations of Ceder and co-workers, support the experimental observations of Bruce and colleagues. The theoretical approach shows that the oxygen ions surrounding these lithium ions can be easily oxidized, in a complementary way, the XAS experiments show that it is the oxygen connected to Mn⁴⁺

that is concerned by the redox process. In summary, the OLi₃Mn₂ octahedra of cations around oxygen play a crucial role in the structure for oxygen oxidation.

The work of the Bruce and Ceder groups — with their complementary experimental and theoretical findings — open new research domains, giving focus to how to design the structure and composition of materials with optimized performance that can increase the capacities on Li-ion batteries. □

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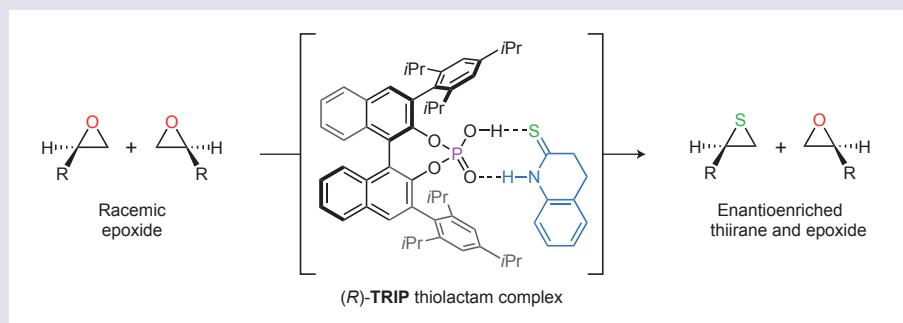
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HETEROCYCLE SYNTHESIS

Back in the ring

Thiiranes — the sulfur-containing counterpart to epoxides — are useful compounds, although they are somewhat difficult to synthesize. With ring strain on the order of 18 kcal mol⁻¹, they can be readily opened to furnish sulfurous organic molecules or polymerized to form high-refractive-index polymers. This ring-strain, while also giving rise to intriguing biological activity, brings with it instability, and methods to synthesize these feisty molecules are limited — unlike their oxygenated brethren. Routes to thiiranes often require harsh reaction conditions that are not amenable to asymmetric synthesis. However, Ben List and co-workers from the Max Planck Institute have developed a method that bypasses both of these limitations with some clever catalysis (*J. Am. Chem. Soc.* **138**, 5230–5233; 2016).

Rather than form the thiirane directly from an olefin or similar, List and co-workers suggest instead starting with the far more accessible epoxides. Noting that thiolactams undergo an exchange reaction with epoxides under acidic conditions — yielding a thiirane and a lactam — the group used chiral phosphoric acid derivatives bearing bulky



triisopropylphenyl groups (TRIP, see figure) to enable a kinetic resolution strategy for the reaction. Because TRIP engages in hydrogen bonding with the thiolactam in a heterodimeric resting state, as observed by *in situ* NMR, the epoxide is directed preferentially to one face of the catalyst. As a result, one enantiomer of the racemic epoxide starting material reacts more rapidly than the other and the products of the reaction are the enantioenriched thiirane and epoxide of opposite handedness, with an average enantiomeric ratio exceeding 97:3.

Owing to the hindered chiral pocket around the acidic phosphate group of TRIP and the low catalyst loading (0.1 mol%),

this method avoids some of the undesired side reactions that typically characterize the acid-catalysed exchange reactions that produce thiiranes. As a result, the reaction has a broad substrate scope, accommodating a wide variety of alkyl and aryl substituents on the parent epoxide. List and co-workers suggest that more convenient access to chiral thiiranes will inspire investigation into their use in synthesis, materials and medicine, where substitution of sulfur in place of oxygen could have dramatic effects on the properties of the product.

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