Lightning fast conduction

In the intensive search for higher performance Li-ion cathode materials the spotlight is firmly fixed on Li-rich compounds. Now, a strategy utilizing a fluorinated, disordered $LiMn_2O_4$ spinel structure shows how ultra-fast Li-ion diffusion and high energy density can be achieved with Mn and O redox.

Robert A. House and Peter G. Bruce

The electric revolution is well underway as we transition from fossil-fuel driven forms of transportation to cleaner, electric vehicles. Advances in lithium-ion battery technology are largely to thank for this; however, the driving range and recharging rate of electric vehicles still falls short of their petrol and diesel counterparts. The energy density, and therefore the range of electric vehicles, is constrained mainly by the cathode material inside the battery. Making improvements to the cathode is a tough materials science challenge. New compounds must be found that can reversibly intercalate and de-intercalate lithium in greater amounts at sufficiently high potential and allow for Li^+ ions to move very quickly through the structure to enable fast charging.

State-of-the-art cathode materials, typically layered compounds, such as $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$, with alternating lithium and transition metal (TM) oxide slabs stacked together, are limited in their ability to intercalate and de-intercalate lithium by the amount of lithium and redox active elements present (that is, $Ni^{2+/3+/4+}$ and $Co^{3+/4+}$). Recent research shows that these limits can be surpassed by substituting some TM ions with extra lithium ions leading to Li-rich compositions such as $Li[Li_{1/6}Ni_{1/4}Mn_{7/12}]O_2$ (ref. [1]). Almost all of the Li^+ ions can be extracted from these materials charge compensated by the participation of the oxide ions, so-called O redox, in addition to the TM ions, leading to higher energy densities than when using TM redox alone[2,3]. However these compounds often exhibit TM migration and O–O bond formation, making them unstable in the charged state. The process of structural reorganization from an ordered to a disordered state during O redox can lead to slow Li^+ diffusion and poor rate performance in a battery. One approach to address the disorder triggered by O redox is to start from an already disordered structure that contains a sufficiently high Li/TM ratio to enable facile Li^+ diffusion pathways. Typical examples are the so-called Li-rich disordered rock salts.

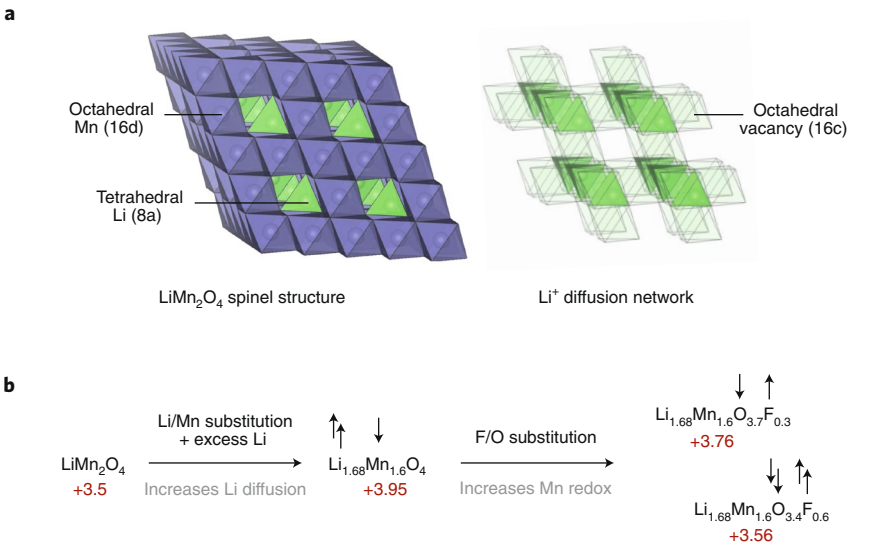

Fig. 1 | Promoting high Li-ion conductivity with spinel-like local structure. a, $LiMn_2O_4$ spinel crystal structure. Li^+ ions diffuse rapidly between face-sharing octahedral 16c and tetrahedral 8a sites. **b**, Modifications to the $LiMn_2O_4$ spinel composition to increase the amount of available lithium and number of facile diffusion pathways whilst balancing Mn and O redox. The oxidation state of Mn is indicated in red, arrows highlight changes in composition.

Writing in *Nature Energy*, Gerbrand Ceder and co-workers demonstrate two Li-rich cathodes, $Li_{1.68}Mn_{1.6}O_{3.7}F_{0.3}$ and $Li_{1.68}Mn_{1.6}O_{3.4}F_{0.6}$, each based on the disordered spinel structure[4]. By tuning the Li/TM and O/F ratios, high energy density from a combination of TM and O redox can be achieved with very high rates. Interestingly, the high rate performance observed in these cathodes is seen in conjunction with O redox, challenging the popular belief that the O redox process is intrinsically sluggish[5].

Spinel and rock salt structures possess the same face centred cubic oxide sublattice. However, spinel structures exhibit cation occupancy of only half the octahedral sites, the rest tetrahedral, whereas the cations occupy exclusively octahedral sites in rock salt. Ordered spinel possesses pathways for Li^+ ion diffusion formed by face sharing 8a (tetrahedral) and 16c (octahedral) sites (Fig. 1a), resulting in very facile Li^+ transport and some of the fastest rates known for cathodes. Despite the disordered spinels distributing Mn into the 16c sites, the Li^+ ion transport is not blocked. The high Li/TM ratio of the disordered spinels provides enough pathways for fast Li^+ transport and exceptionally fast rates of charge and discharge. Fluorination lowers the manganese oxidation state (Fig. 1b), increasing the capacity from TM redox. Furthermore, half of the capacity arises from O redox, which is reversible and fast, although some voltage hysteresis between charge and discharge remains.

In a wider context, the disordered spinels reported by Ceder and co-workers may bear some similarity to those that form on cycling layered $LiMnO_2$, which can also be charged and discharged many times over a wide composition range unlike the ordered spinels. They also relate to ordered spinels

such as $Li_4Mn_5O_{12}$, which have Li on the Mn 16d sites[6].

High rates in porous composite electrodes depend on a number of factors. As well as facile Li^+ transport inside the particles, Li^+ diffusion within the electrolyte inside the pores (between the particles) and efficient electron exchange between particles across the cathode are important. Ceder and team's experiments were performed with high carbon and low mass loadings, so that the intrinsic rate of the disordered spinels could be studied. It will be interesting to see how the disordered spinels perform with typical practical loadings and carbon content. Following on from this work, investigation of more scalable synthetic methods for making these compounds than high energy ball-milling, and how to suppress the capacity fading observed, merit further attention. Nevertheless, the important results presented in the study of Ceder and co-workers demonstrate that very high rates are possible with oxyfluoride spinels, challenging the belief that O redox is a slow process.

Department of Materials, University of Oxford, Oxford, UK.
✉*e-mail: peter.bruce@materials.ox.ac.uk*

References

1. Zhonghua, L., Beaulieu, L. Y., Donaberger, R. A., Thomas, C. L. & Dahn, J. R. *J. Electrochem. Soc.* **149**, A778–A791 (2002).
2. Luo, K. et al. *Nat. Chem.* **8**, 684–691 (2016).
3. Seo, D. H. et al. *Nat. Chem.* **8**, 692–697 (2016).
4. Ji, H. et al. *Nat. Energy*. https://doi.org/10.1038/s41560-020-0573-1 (2020).
5. Assat, G. & Tarascon, J.-M. *Nat. Energy* **3**, 373–386 (2018).
6.