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Energy Materials

Topology to improve battery technology

Eric McCalla* and Shipeng Jia

Department of Chemistry, McGill University, Montreal, Canada

*Corresponding author: eric.mccalla@mcgill.ca

Standfirst

Both lithium-ion batteries and their sodium-ion counterparts have the opportunity to play an important role in combating climate change but often suffer structural instabilities in the cathodes that degrade performance. Now a study on two cathode materials that can function in either battery type sheds light on how their structure should be designed to suppress these instabilities.

Main text

The growing global demand for lower emissions to help address climate change is setting unprecedented criteria for a number of advanced technologies. In the context of batteries, two important green applications, electric vehicles (EVs) and grid storage, are pushing the limits of modern batteries in terms of both energy density (e.g. to increase the driving range of EVs) and battery cycling (e.g. to lengthen the lifespan). Typically, when a battery material is engineered to maximize the amount of energy it can store, the long-term performance suffers. It has become necessary to design advanced materials that can both store large quantities of energy and maintain their structural stability during battery operation in order to enable good performance for years and hopefully soon multiple decades. The state-of-the-art high energy batteries are undeniably lithium-ion batteries with layered mixed transition metal oxides as the cathodes with the structure as illustrated in Figure 1. Since the first report in the 1980s, this class of cathode has been known to be plagued by subtle structural transformations during battery operation that involve solely the shearing of layers during lithium removal and reinsertion. For example, LiCoO₂, the first commercialized cathode, undergoes a phase transition from the so-called O3 layered structure to O1 as shown in Figure 1. This transition is reversible but leads to disastrous energy loss upon continued cycling (e.g. a loss of 43% in about 1 month of use ¹). In commercial batteries, coatings and substitutions are tested means that can effectively suppress such transformations. For instance, NMC cathodes with co-substitution of Ni and Mn for Co turn out to be robust against the structural change and can retain 98% of the initial capacity retention after 100 cycles². However, there remains no fundamental understanding as to why certain compositions are granted immunity from the shearing of the layers. Furthermore, the NMC cathodes rely on nickel and cobalt both of which raise substantial sustainability concerns in terms of both their limited natural reserves and high toxicity.

More recently, next-generation cathodes have been developed with excess Li giving rise to the socalled Li-rich oxides with stoichiometry $\text{Li}_{1+x}M_xO_2$ where M can be mixtures of transition metal elements.³ These materials rely on both transition metal redox and oxygen redox to enable a larger energy density than traditional cathodes.⁴ Although oxygen redox can increase the energy density, it is often times poorly reversible and finding structures that stabilize reversible oxygen redox is an on-going challenge. Similarly, some Li-rich oxides undergo the O3 to O1 conversion and it again results in massive capacity loss with cycling.⁵ The Li-rich cathodes also suffer from a decrease in average voltage as the battery is used for multiple cycles and this feature is currently preventing commercialization.⁶

Now writing in *Nature Sustainability*, Gao and co-workers⁷ explore these important issues by studying two materials that have the same compositions (Na_{0.6}Li_{0.2}Mn_{0.8}O₂) but crystallize in different structures. The two polymorphs (called P2 and P3) differ solely in how the fully ordered layers are stacked as shown in Figure 1. These materials have a number of features that make them of high interest. From the sustainability standpoint, they are composed solely of earth-abundant benign elements, making them advantageous over commercial NMC cathodes. Furthermore, these cathodes can be used either in a Na-ion battery (Na is removed and reinserted during battery use) or a Li-ion cell (Na is first removed, then replaced with Li). Although the performance as a Naion cathode is not competitive with the state-of-the-art, the performance as a Li-rich cathode is quite promising. With a high reversible capacity of 240 mAh g^{-1} and negligible capacity loss over hundreds of cycles, the P3 polymorph is highly competitive for next-generation Li-ion batteries (e.g. 230–250 mAh g⁻¹ achieved in previously reported Li-rich cathodes ^{3,4}). Most interestingly, the oxygen redox is reversible in both the P2 and P3 materials, but the extended cycling is far better in the P3 polymorph and this is yet again associated with the suppression of shearing of layers.

Since the layers in the P2 and P3 polymorphs are identical and highly ordered, it is possible to track the topology change during battery operation. Gao and colleagues identify a stacking sequence that serves to suppress the shearing. To further quantify the stacking sequence, the authors then introduce a parameter, topological order, which in the case of P2 is associated with

poor cycling whereas for P3 it leads to long-term reversibility such that P3 is termed to be topologically protected. This represents a successful correlation of topology to structure stability in these materials and certainly warrants further development.

Although the authors propose that the concept can be extended to more disordered materials such as those used commercially, it remains to be seen if a useful order parameter can be determined for structures with significant disorder on the layers where stacking faults become abundant. There also remains a considerable amount of work before the topological order parameter approach can be developed to the point where it can predict whether or not a particular stacking sequence will be beneficial for battery operation. It is also of note that both the P2 and P3 materials show significant voltage fade when used as a Li-rich cathode, which means that topological protection does not seem to be a solution to this particular problem in these next-generation cathodes. Thus, further research on these highly ordered materials to understand the mechanisms behind voltage fade is needed.

The insights into the importance of topological order in stabilizing structures during battery use, presented in *Nature Sustainability*⁷, are substantial in that they provide a potential way to finally predict what structures will not undergo a detrimental mechanism that has plagued Li-ion cathodes for over 40 years. We now need more work to determine if this approach can be used in materials where there is more disorder on the layers therefore making the stacking sequences far more complex to determine and quantify. Such disorder is currently present in all commercialized Li-ion cathodes that have the layered oxide structure.

References

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Figure 1: Impact of structural transformation in cathodes on battery performance. The original Li-ion cathode (LiCoO₂) shows layer shearing during charging (removal of Li) and this leads to gradual loss in performance over multiple cycles. Substitutions and/or coatings are typically utilized to suppress these transformations. By contrast, the P2 and P3 cathodes reported by Gao et al ⁷ demonstrate that shearing can be suppressed during charging without substitutions nor coatings. Instead, topological protection from the relative positions of the Li atoms can prevent transformation during battery operation.