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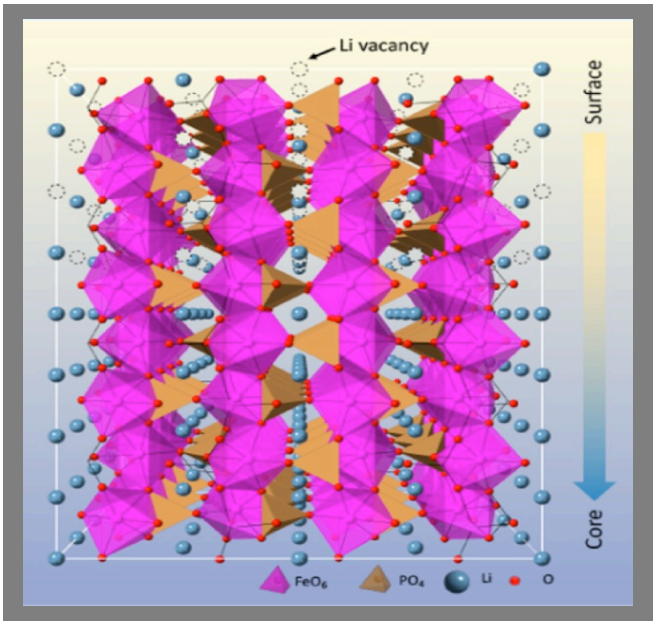
Understanding the surface structure in $LiTMPO_4$ Cathodes

Rechargeable batteries are ubiquitous in the devices of the modern world. The technological demand is to produce new battery materials that can store more electrical energy in as small a volume as possible and that can be charged and discharged many times without degrading the amount of electricity that can be stored. A current commercial battery material is $LiFePO_4$. The Fe atom can be replaced by other transition metal (TM) elements to potentially vary the electrical properties of this material.

Describe the Research & Outcomes

The $LiTMPO_4$ material produces a regular crystalline structure known as olivine. At the atomic level, this structure produces channels through which the lithium ions can move. The materials role is to be able to release its lithium ions when the cell is electrically charged. The lithium ions physically move out of this and through a liquid transport medium before entering into a solid anode. As the lithium leaves, the essential physical structure remains in place and the transition metal ion will change its charge state from +2 to +3 to account for the loss of the Li ion. Once all the lithium ions have left the structure, the material is now chemically $TMPO_4$ and the battery is fully charged. Discharging the battery and the lithium ions have to move back into the structure to reform the $LiTMO_4$. By replacing the transition metal TM atom from Fe to Mn, Co or Ni the intrinsic voltage produced by the battery increases. A higher voltage, with all other things being equal, indicates better energy storage. Whilst at the atomic scale the material allows the movement of the lithium ions the material is produced in particle sizes of 200 to 500 nm. Lithium transport through the $LiTMPO_4$ is conceptually "easy" however at the interface between the particle and the liquid how the lithium moves out, that is less well known. This study used XPS, Raman and soft X-ray Absorption Spectroscopy



$LiFePO_4$ Proposed Surface structure showing Li vacancies

(sXAS) to look at the surface interface of the $LiTMPO_4$ particles. sXAS, in conjunction with the other techniques, was able to show that at the surface of the particles there is a layer of lithium depleted $LiTMPO_4$ with the presence of transition metal atoms in a permanent 3+charge state. In this particular study, the effect of this layer on the electrical properties of any particular battery performance cannot be shown, but it is important to know that this layer exists when trying to understand the performance of real battery prototypes.

Describe the Benefits & Impacts

Battery materials rely on the physical transport of ions within the battery. All batteries will have many interface regions between the different constituent materials. Often it is at these interface regions where the reactions occur that limit the electrical performance achieved by the battery and even its longer-term failure. The soft X-ray beam line allows researchers an additional tool to investigate the surfaces of their battery materials and can give insights that will lead to better batteries in the future.

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