**Surface Li-depletion and the electronic band structure of olivine phosphates**

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**Introduction**

Lithium transition metal phosphates (LTMP) LiMPO4 (M=Fe, Mn, Co, Ni) constitute a promising family of cathode materials for Li-ion batteries (Padhi et al. 1997; Zaghib et al. 2008). Li depletion on the surface and the electronic band structure for very carefully synthesised LFeP have previously been thoroughly characterized and discussed (Zhang et al. 2019). In this research, the investigation of surface Li depletion is extended to a wider range of LTMP compounds.

**Methods**

Carefully synthesized, XRD-phase pure LTMP samples were further characterized using X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) and soft X-ray absorption spectroscopy (sXAS) at the Australian Synchrotron. Optical gaps were estimated from UV-Vis-NIR diffusion reflectance spectra. Electronic structure calculations were conducted within the framework of first principles density functional theory (DFT), as implemented in the CASTEP module of Material Studio 2017.

**Results and discussion**

High-resolution TM-2p XPS and O-K XAS edge spectra are displayed in Figs. 1a and 1b, respectively. The presence of TM3+ ions is observed on the surface of all the LTMP particles, indicating Li-depletion in order to have charge neutrality. The relative intensity changes of the pre-edge features in the O-K edge (Fig. 1b) from surface to core also suggest the presence of Li-depletion on the surface. Extended Urbach tails are observed in the Tauc plots of LMnP and LFeP, while sharper optical absorption edges at 4.6 and 5.1 eV are obtained for LCoP and LNiP, in addition to intermediate absorption peaks from 0.5 to 3 eV (Fig.1c). Surface Li-depletion introduces localized impurity states, which are responsible for the Urbach tails, shifts in absorption edges and intermediate absorption peaks in the optical measurements.

(a)

(b)

(c)

**Fig. 1.** (a) High-resolution TM-2p XPS, (b) O-K edge spectra, (c) optical absorption and Tauc plots for the LTMP samples.

**Conclusion**

The presence of surface Li-depletion for all carefully synthesised LTMP samples is confirmed by both XPS and sXAS. DFT calculations are re-evaluated according to the optical absorption spectra. Surface Li-depletion is responsible for extended Urbach tails, shifts in the absorption edges and absorption peaks before the band edge in optical measurements.

**References**

1. Padhi, A. K., et al. (1997), *Journal of the Electrochemical Society 144 (4)*, 1188-1194.

2. Zaghib, K., et al. (2008), *Chemistry of Materials* *20 (2)*, 462-469.

3. Zhang, Y., et al. (2019), *RSC Advances* *9 (2)*, 1134-1146.