

New Tavorite-type Compositions as Positive Electrode Materials for Lithium-ion Batteries

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Polyanionic materials attract a strong interest in the field of Li-ion battery research. Tavorite-type compositions offer a very rich crystal chemistry, among which LiVPO_4F has the highest theoretical energy density (i.e. 655 Wh/kg). New Tavorite-type compositions were obtained: LiVPO_4OH and $\text{LiVPO}_4\text{F}_{1-y}\text{O}_y$, for these latter by direct syntheses or by aging upon oxidation in air. We will show how we can tailor the structure, the potential and the reaction mechanism involved, playing with the composition of the Tavorite-type phases. IR and NMR spectroscopies are obviously key characterization tools to identify the nature of the phase formed, with a clear signature for vanadyle and hydroxyl bonds, and to discriminate between defects and impurities. Electrochemical tests reveal original properties during the charge of LiVPO_4OH . Li^+ and H^+ are extracted from the structure at the same equilibrium potential (3.95 V vs Li^+/Li): the formation of the intermediate V^{4+} -rich phase is not observed whereas VPO_4O is obtained at the end of the charge. This system interestingly illustrates one possible track to follow to develop two-electron reactions at the same potential, playing with the stability of the antagonist bond in order to promote the concomitant and reversible extraction/reinsertion of two alkalis. In addition, we will also discuss how detrimental/positive the defects can be on the electrochemical properties of the mixed oxy-fluorophosphates $\text{LiVPO}_4\text{F}_{1-y}\text{O}_y$.

Acknowledgements

This research is performed in the frame of the French network RS2E (<http://www.energie-rs2e.com>) and of the European network ALISTORE-ERI (<http://www.alistore.eu>).