High Voltage Li-ion Cathode Based on Substituted LiCoPO$_4$
High Voltage Li-ion Cathode Based on Substituted LiCoPO₄

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To further increase the energy density of the state-of-the-art safe 3.4 V olivine lithium iron phosphate (LFP) based Li-ion batteries, 4.8 V lithium cobalt phosphate (LCP) has been explored and studied. The structure of LiCoPO₄ is shown in Fig. 1 and a comparison of the discharge voltage of LiCoPO₄ to the discharge voltage of the isostructural LiFePO₄ is shown in Fig. 2. However, LCP suffers from lower conductivity than LFP. Furthermore, the voltage of LCP is higher than the oxidation stability limit of the state-of-the-art electrolyte made of LiPF₆ in ethylene carbonate (EC) and ethylmethyl carbonate (EMC) mixtures.

Initial results on LCP showed low capacity utilization and a severe loss of discharge capacity upon multiple charge-discharge cycles. For example, Amine et al. observed a capacity utilization of 0.42 Li per LCP and Wolfenstine et al. observed a capacity utilization of 0.6 Li. Tadanga et al. observed a 10th cycle discharge capacity of ~52% of the initial capacity, Brannik et al. reported ~59% and Wolfenstine et al. reported ~53% capacity retention (This has been attributed to irreversible structural changes or amorphization of the charged, low-lithium content material and electrolyte degradation.

Using Fe substitutionally-modified LCP (Fe-LCP), the capacity utilization was improved to 0.7 Li and the capacity retention was substantially improved in conjunction with an electrolyte additive that improves the electrolyte stability at high voltage as we reported recently. With further substitution as designated as Gen2 s-LCP, we further improved the capacity utilization to 0.78 Li and rate capability. Our Gen3 s-LCP shows further improvement in coulombic efficiency at >99% cycling as shown in Fig. 3.

References

![Figure 1: Structure of LiCoPO₄](image1)

![Figure 2: Illustration of the voltage difference between LiFePO₄ and and substituted LiCoPO₄](image2)
Figure 3 Capacity and coulombic efficiency of Gen2 and Gen 3 s-LCPs.