

Substituted  $\text{LiCoPO}_4$  as Li-ion Cathode

Jan L. Allen<sup>1</sup>, Samuel A. Delp<sup>1</sup>,  
T. Richard Jow<sup>1</sup> and Jeff Wolfenstine<sup>1</sup>

<sup>1</sup>Electrochemistry Branch, Army Research Laboratory  
2800 Powder Mill Road, Adelphi, MD 20783

There is strong interest in electrode materials for Li-ion batteries that function near 5 V for their high energy storage potential. With this in mind,  $\text{LiCoPO}_4$  has been thought of as a promising cathode material owing to its high discharge voltage of around 4.8 V.<sup>1</sup> The structure of  $\text{LiCoPO}_4$  is shown in figure 1 and a comparison of the discharge voltage of  $\text{LiCoPO}_4$  to the discharge voltage of the isostructural  $\text{LiFePO}_4$  is shown in figure 2. Initial results on  $\text{LiCoPO}_4$  showed a severe loss of discharge capacity upon multiple charge-discharge cycles. For example, Tadanga et al.<sup>2</sup> observed a 10th cycle discharge capacity of ~52% of the initial capacity, Bramnik et al.<sup>3</sup> reported ~59% and Wolfenstine et al.<sup>4</sup> reported ~53% capacity retention (This has been attributed to irreversible structural changes or amorphization of the charged, low-lithium content material and electrolyte degradation).

Our more recent work<sup>5</sup> reported improved capacity retention using substitutionally-modified  $\text{LiCoPO}_4$  in conjunction with an electrolyte additive<sup>6</sup> that improves the electrolyte stability at high voltage. Our related work<sup>7</sup> compared the electronic structure of  $\text{LiFePO}_4$  and  $\text{LiCoPO}_4$  through spectroscopic and electronic methods in order to understand the differences in electrochemical performance.

Herein we will present results showing further improvements to the electrochemical performance of substituted  $\text{LiCoPO}_4$  including higher discharge capacity and improved cycle life. We will discuss alternative scalable synthesis methods, substitutional chemistry of  $\text{LiCoPO}_4$  and performance enhancements that result from reformulating the electrolyte.

## References

1. K. Amine, H. Yasuda and M. Yamachi, *Electrochem. Solid State Lett.*, **3**, 178 (2000).
2. K. Tadanaga, F. Mizuno, A. Hayashi, T. Minami and M. Tatsumisago, *Electrochemistry*, **71**, 1192 (2003).
3. N.N. Bramnik, K.G. Bramnik, T. Buhrmester, C. Baehtz, H. Ehrenberg and H. Fuess, *J. Solid State Electrochem.* **8**, 558 (2004).
4. J. Wolfenstine, U. Lee, B. Poesse and J.L. Allen, *J. Power Sources*, **144**, 226 (2005).
5. J.L. Allen, T.R. Jow and J. Wolfenstine, *J. Power Sources*, 196 (2011) 8656.
6. A. V. Cresce, A.V and K. Xu, *J. Electrochem. Soc.* **158**, A337, 2011.
7. M.D Johannes, K. Hoang, J.L. Allen and K. Gaskell, *Phys. Rev. B* **85**, 115106 (2012).

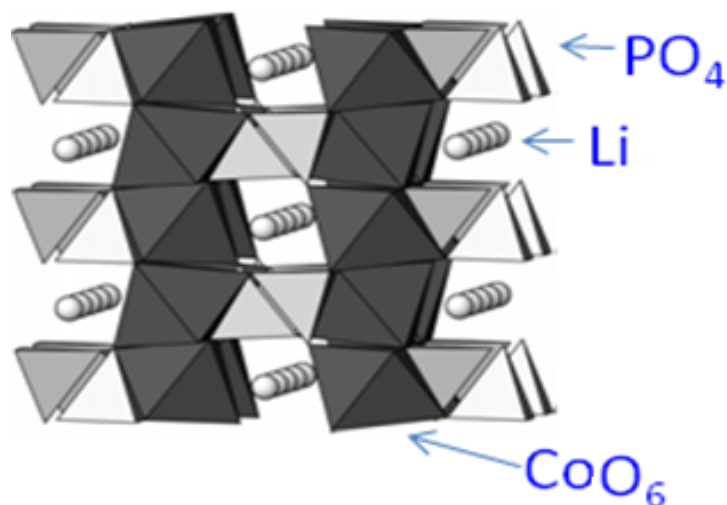


Figure 1: Structure of  $\text{LiCoPO}_4$

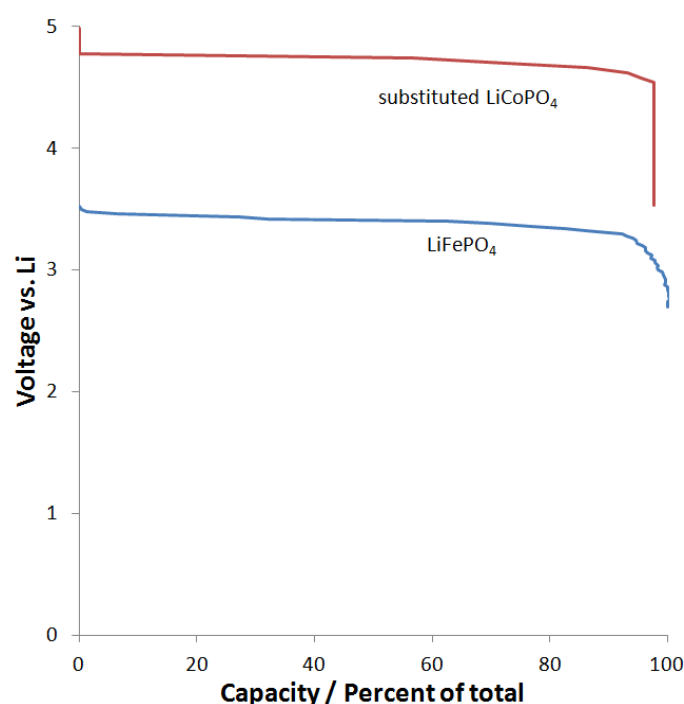


Figure 2. Illustration of the voltage difference between  $\text{LiFePO}_4$  and substituted  $\text{LiCoPO}_4$ .