

## In Situ NMR Study of a $\text{Cu}_3\text{P}$ Lithium Battery

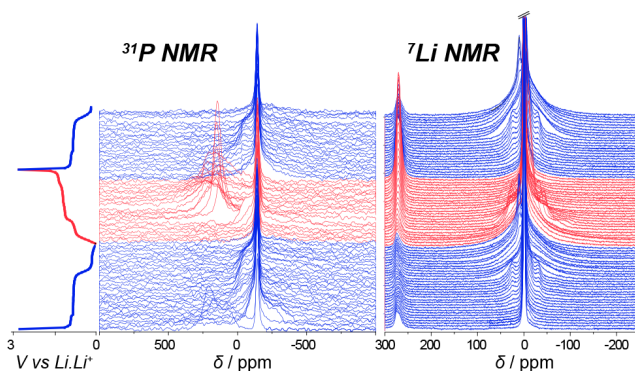
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In a quest for high capacity electrodes for lithium-ion secondary batteries, copper phosphide ( $\text{Cu}_3\text{P}$ ) has previously been investigated by *in situ* (real-time) XRD<sup>2</sup> as a possible negative electrode and demonstrated its good electrochemical performances.<sup>1</sup> However, the complete electrochemical mechanisms  $\text{Cu}_3\text{P} \rightleftharpoons \text{Li}_3\text{P}$  was not completely understood. For example, the expected final phase  $\text{Li}_3\text{P}$  was not detected by XRD. For this reason, different analytical techniques should be considered to obtain complementary information and deduce the mechanism of the electrochemical reaction of  $\text{Cu}_3\text{P}$  with lithium. Moreover, since  $\text{Cu}_3\text{P}$  is a conversion material and that therefore metastable  $\text{Li}_x\text{Cu}_{3-x}\text{P}$  phases are formed during the potential cycling; consequently, *in situ* characterization is a preferable approach since the electrochemical reactions might evolve when the battery is stopped and dismantled for *ex situ* analyses.



This study reports a multinuclei *in situ* NMR spectroscopic characterization of the electrochemical reactions of a  $\text{Cu}_3\text{P}$  electrode towards lithium. Taking advantage of the different nuclear spin characteristics, we have obtained real-time  $^{31}\text{P}$  and  $^7\text{Li}$  NMR data for a comprehensive understanding of the

electrochemical mechanism during the discharge ( $\text{Cu}_3\text{P} \rightarrow \text{Li}_3\text{P}$ ) and charge ( $\text{Li}_3\text{P} \rightarrow \text{Cu}_3\text{P}$ ) processes. The large NMR chemical shift span of  $^{31}\text{P}$  facilitates the observation of the chemical evolutions of the different lithiated and delithiated  $\text{Li}_x\text{Cu}_{3-x}\text{P}$  phases; whereas the quadrupolar line features in  $^7\text{Li}$  enables the identification of the asymmetric Li sites. These combined NMR data offer an unambiguous identification of four distinct  $\text{Li}_x\text{Cu}_{3-x}\text{P}$  phases –  $\text{Li}_3\text{P}$ ,  $\text{Li}_{0.2}\text{Cu}_{2.8}\text{P}$ ,  $\text{Li}_2\text{CuP}$  and  $\text{Cu}^0$ -intercalated  $\text{Li}_2\text{CuP}$  – and the characterization of their involvements in the electrochemical reactions. The study suggests that the presence of  $\text{Cu}^0$ - $\text{Li}_2\text{CuP}$  in the charge reaction might be responsible for the poor capacity retention in  $\text{Cu}_3\text{P}$  lithium battery when cycles to a ‘low’ voltage potential.<sup>1</sup>

### References

1. Stan, MC. et al., *Adv. Energy Mat.* 2013, **3**, 231.
2. Mauvernay, B. et al., *J. Phys. Chem. Solids* 2006, **67**, 1252.