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In Situ NMR Study of a Cu_3P Lithium Battery

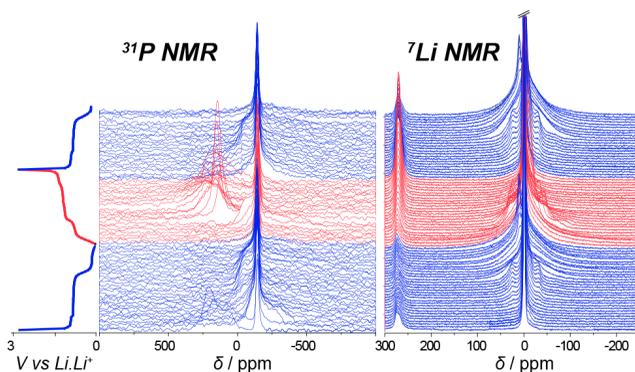
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In a quest for high capacity electrodes for lithium-ion secondary batteries, copper phosphide (Cu_3P) has previously been investigated by *in situ* (real-time) XRD² as a possible negative electrode and demonstrated its good electrochemical performances.¹ 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 Li_3P 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 Cu_3P with lithium. Moreover, since Cu_3P 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 Cu_3P electrode towards lithium. Taking advantage of the different nuclear spin characteristics, we have obtained real-time ^{31}P and ^7Li 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}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 ^7Li 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 – Li_3P , $\text{Li}_{0.2}\text{Cu}_{2.8}\text{P}$, Li_2CuP and Cu^0 -intercalated Li_2CuP – and the characterization of their involvements in the electrochemical reactions. The study suggests that the presence of Cu^0 - Li_2CuP in the charge reaction might be responsible for the poor capacity retention in Cu_3P lithium battery when cycles to a ‘low’ voltage potential.¹

References

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