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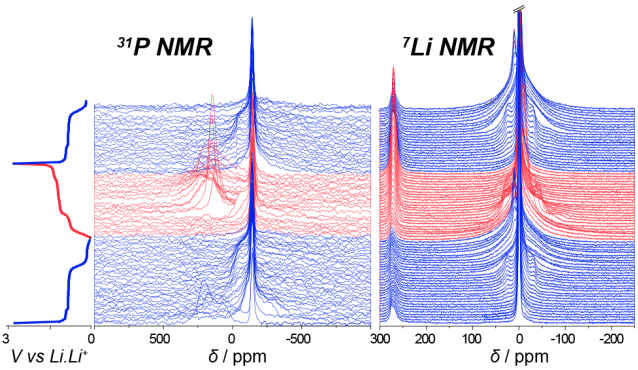
In a quest for high capacity electrodes for lithium-ion secondary batteries, copper phosphide (Cu_3P) has previously been investigated by in situ (real-time) XRD[2] as a possible negative electrode and demonstrated its good electrochemical performances.[1] However, the complete electrochemical mechanisms $Cu_3P \rightleftharpoons Li_3P$ 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 $Li_xCu_{3-x}P$ 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 ^{7}Li NMR data for a comprehensive understanding of the electrochemical mechanism during the discharge ($Cu_3P \rightarrow Li_3P$) and charge ($Li_3P \rightarrow Cu_3P$) processes. The large NMR chemical shift span of ^{31}P facilitates the observation of the chemical evolutions of the different lithiated and delithated $Li_xCu_{3-x}P$ phases; whereas the quadrupolar line features in ^{7}Li enables the identification of the asymmetric Li sites. These combined NMR data offer an unambiguous identification of four distinct $Li_xCu_{3-x}P$ phases – Li_3P, $Li_{0.2}Cu_{2.8}P$, 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.