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In Situ NMR Study of a Cu_3P Lithium Battery

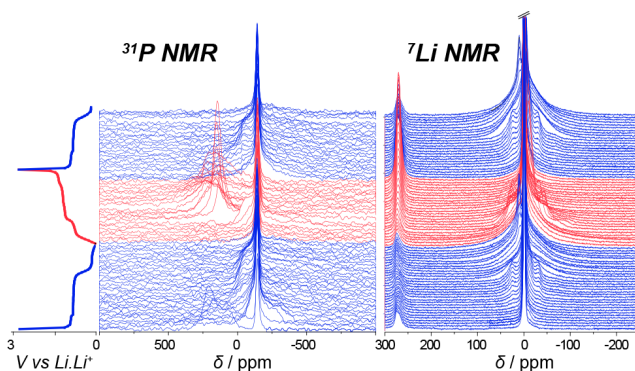
Alan Wong^{a*}, Fabrizia Poli^b, Laure Monconduit^c, and Michel Letellier^d

a, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette, France

b, Centre de Recherche sur la Matière Divisée, FRE 3520 CNRS, 1b rue de la Férellerie, 45071 Orléans, France

c, Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, UMR 5072 CNRS, Institut Charles Gerard, Université Montpellier 2 Cedex 05, 34095 Montpellier, France

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.