

**Dual reaction mechanism –
combining insertion and conversion**
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Nowadays, one of the main challenges in the battery field is the limited specific energy of commercial Li-ion batteries. One option to overcome this challenge is to increase the specific charge of battery materials. Traditionally, insertion materials like graphite, LiFePO_4 or LiCoO_2 are used. All those materials have in common that they react with maximum 1 lithium ion per formula unit. Therefore, their specific charges are limited. Conversion materials like Si, Sn and others react with much more lithium ions per formula unit. However, the higher specific charge of those materials is “bought” with major structural changes in the material including large volumetric changes, both resulting in high electrochemical overpotentials and a significant charge loss with cycle number.

In 2005 Belharouak and Amine reported $\text{Ni}_{0.5}\text{TiOPO}_4$ as a high specific charge material (422 Ah/kg) [1]. In 2009 Essehli *et al.* showed that the isostructural $\text{Co}_{0.5}\text{TiOPO}_4$ is also electrochemically active with a similar specific charge (434 Ah/kg) [2]. Since other members of the $\text{M}_{0.5}\text{TiOPO}_4$ -family like $\text{Cu}_{0.5}\text{TiOPO}_4$ and $\text{Fe}_{0.5}\text{TiOPO}_4$ are isostructural, they are as well potential candidates as battery materials. The specific charge for all of them is higher than expected from the vacant sites in the structure. The existence of vacant sites in the structure that can be occupied by lithium is typical for insertion materials. But the fact that the specific charge is higher than the available sites for lithium ions might indicate also a conversion reaction. Therefore, it is worth to study the mechanism during lithiation and delithiation.

We selected $\text{Cu}_{0.5}\text{TiOPO}_4$ and $\text{Fe}_{0.5}\text{TiOPO}_4$ for detailed investigations. Figure 1 shows their respective galvanostatic curves upon lithiation and delithiation. The reaction upon lithiation is with up to 5 lithium ions per formula unit (≈ 700 Ah/kg) and for delithiation with approximately 3 lithium ions per formula unit. The following cycles show a reversible process with more than 2 Li ions per formula unit. A GITT measurement of the first cycle of both samples was performed in order to determine which reaction mechanisms (insertion/conversion) occur and at which thermodynamic potential the reactions occur (Figure 2). It is clearly visible that both reaction mechanisms are a combination of insertion and conversion processes. Investigations on the reaction mechanism based on *ex situ* and *in situ* synchrotron XRD, XAS, SQUID, SEM, ^{31}P MAS NMR and TEM were carried out and support this hypothesis. As an example, the *in situ* XRD of $\text{Fe}_{0.5}\text{TiOPO}_4$ as active material (Figure 3) shows that first a new phase is formed with slightly modified structural parameters (insertion process) and then the material turns amorphous (as it is not unusual for a conversion material). Full reaction mechanism will be presented and discussed for both samples.

Acknowledgement:
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Literature:
[1] I. Belharouak, K. Amine, *Electrochem. Commun.* 2005, 7, 648.
[2] R. Essehli et al., *Mater. Res. Bull.* 2009, 44, 817.

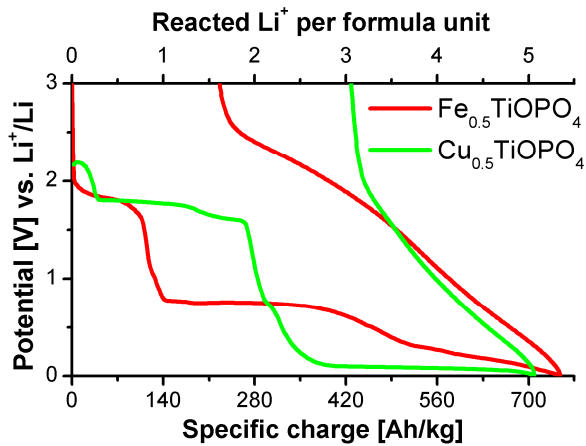


Figure 1: Galvanostatic curves of $\text{Fe}_{0.5}\text{TiOPO}_4$ and $\text{Cu}_{0.5}\text{TiOPO}_4$ in the 1st cycle at C/10 rate.

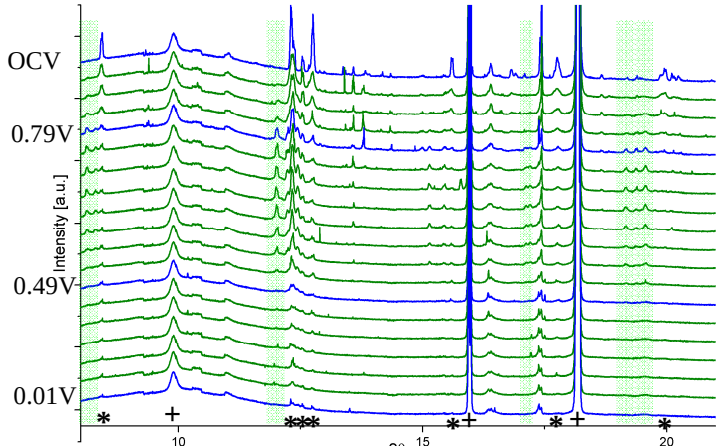


Figure 3: *In situ* XRD of $\text{Fe}_{0.5}\text{TiOPO}_4$ (the main reflexes of $\text{Fe}_{0.5}\text{TiOPO}_4$ are indicated with *, reflexes of the cell are indicated with +).

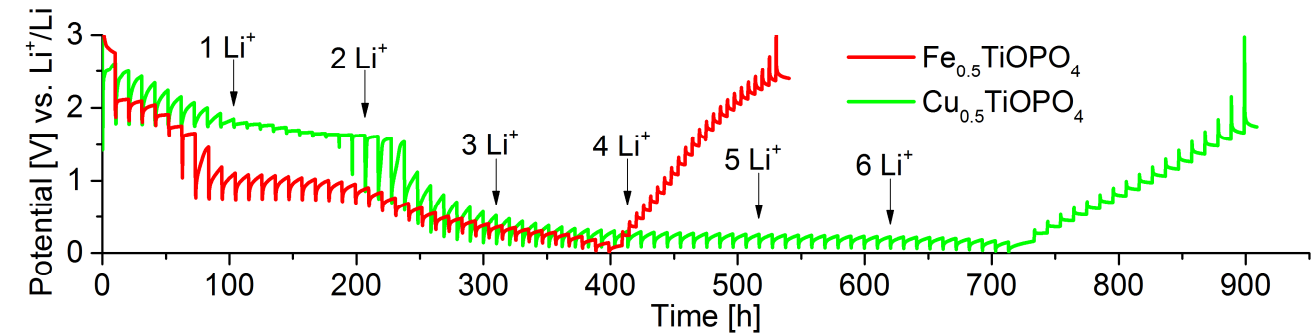


Figure 2: GITT of $\text{Fe}_{0.5}\text{TiOPO}_4$ and $\text{Cu}_{0.5}\text{TiOPO}_4$.