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Mechanism of lithium insertion-extraction in metallophosphates with olivine-like structure

Natalia Bramnik, K. Nikolowski, C. Baehtz^a

Institute for Materials Science, Darmstadt University of Technology, Darmstadt, Germany, ^aHasylab/DESY, Hamburg, Germany. E-mail: bramnik@tu-darmstadt.de

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The development and commercialisation of the LiFePO_4 -cathode for lithium ion batteries provoked the strong interest to the other members of the olivine-like metallophosphates family LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$). It is well known that lithium extraction from LiFePO_4 (triphylite) leads to the formation of the new phase FePO_4 (heterosite), which is isostructural to the pristine compound [1]. By the in-situ synchrotron diffraction we studied the structural changes occurring at the delithiation of $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ and LiCoPO_4 . The extraction of lithium from $\text{LiMn}_{0.6}\text{Fe}_{0.4}\text{PO}_4$ proceeds as a two-step process [2]. The first step (ca. 3.6 V vs. Li/Li^+) corresponds to the oxidation of iron ($\text{Fe}^{2+}/\text{Fe}^{3+}$), the second one (ca. 4.1 V vs. Li/Li^+) to the oxidation of manganese ($\text{Mn}^{2+}/\text{Mn}^{3+}$). In contrast to the mechanism earlier reported for this compound [3], both reactions were revealed to proceed in two-phase manner. A solid solution domain seems to exist in the intermediate state, where $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrochemical reaction ends and $\text{Mn}^{3+}/\text{Mn}^{2+}$ begins. All phases appearing during charging the cell have the same olivine-like structure with different cell parameters. The two step character of lithium extraction for LiCoPO_4 was observed also and confirmed by XAS measurements [4, 5]. In in-situ diffraction experiments on LiCoPO_4 reveal the formation of lithium-poor olivine-like phase at the earlier stage of charge.

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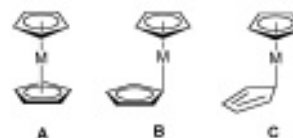
The Structural Diversity of Zincoenes: Half-Sandwich, Slipped-Sandwich and Dimetalloenes Structures

Ernesto Carmona, Irene Resa and Amor Rodriguez

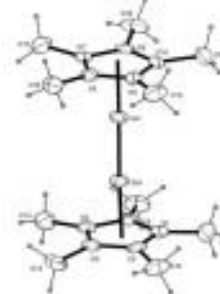
Instituto de Investigaciones Químicas y Departamento de Química Inorgánica. Universidad de Sevilla y Consejo Superior de Investigaciones Científicas. Avda. Américo Vespucio, 49. 41092 Sevilla, Spain. E-mail: guzman@us.es

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In contrast to the metallocenes of the transition metals, bis(cyclopentadienyl) derivatives of the nontransition elements may adopt different structures that, in addition to the classical sandwich geometry **A** (or the analogous distribution of D_{5h} eclipsed molecular symmetry) encompass the η^5/η^1 structures **B** and **C**. The former, or slipped-sandwich geometry, $\eta^5/\eta^1(\pi)$, is characterized, among other features, by nearly parallel cyclopentadienyl rings, whereas in the latter the monohapto ring is coordinated to the metal in the usual sigma fashion ($\eta^5/\eta^1(\sigma)$ structure).



In this contribution our structural studies on zincoenes will be discussed. It has been found that while the peralkylated cyclopentadienyl ligands C_5Me_5 ,^[1] $\text{C}_5\text{Me}_4\text{Bu}^f$, and others, give rise to ZnCp'_2 metallocenes of the slipped-sandwich type, **B**, the silyl-substituted $\text{C}_5\text{Me}_4\text{SiMe}_3$ ligand allows the adoption of the $\eta^5/\eta^1(\sigma)$ geometry, **C**.^[2] In addition, a unique dizincocene complex $\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2$ has been isolated and shown to consist of two metal-metal bonded ($\eta^5\text{-C}_5\text{Me}_5$)Zn units, with a short Zn-Zn distance of 2.31 Å.^[3]



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