

LITHIUM IRON METHYLENE DIPHOSPHONATE, A NEW ORGANIC-INORGANIC HYBRID MATERIAL FOR LI-ION BATTERIES.

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The research on positive electrode materials for Li-ion batteries has generally been focused on inorganic compounds. Introducing an organic component into the inorganic framework would open various new synthetic possibilities and might allow to adjust the electrochemical properties of the metal ions by the influence of neighboring organic groups. $[\text{Fe(III)(OH)}_{0.8}\text{F}_{0.2}(\text{bdc})]\cdot\text{H}_2\text{O}$ is the first hybrid organic-inorganic materials reported to be active in positive electrode for Li-ion batteries,¹ and so far only few more examples of such electroactive hybrid materials are known in the literature.

To introduce a new class of organic-inorganic hybrid materials for Li-ion batteries with versatile organic parts, we chose to investigate transition metal diphosphonates. The material lithium iron methylene diphosphonate (LFMD) was selected as reference material as proof of concept for hybrid materials for positive electrode in Li-ion batteries. LFMD was synthesized by a simple hydrothermal route, yielding a material with a new crystalline phase. In a half-cell configuration, it exhibits a specific charge of 90 mAh/g upon lithiation, which remains stable for more than 100 cycles (Figure 1). The specific charge even continuously increases after 60 cycles to reach a value of 118 mAh/g after 160 cycles. The large irreversibility of the first and the second cycle with a different potential profile is assumed to originate from the removal of residual H^+ in the structure upon delithiation, leading to enhanced electrolyte decomposition. The consecutive delithiation steps do not any longer show this feature, thereby increasing the coulombic efficiency drastically from very low in the first cycle (~ 40%) to a more reasonable value (> 90%) after 10 cycles, reaching a stable value of 97% after 50 cycles. *Operando* XANES confirmed the oxidation and reduction of iron during the cycling.

The results obtained provide a basis for investigations on the influence of different heteroatoms or organic entities substituted to the diphosphonate on the electrochemistry of the hybrid material, which is the focus of our future research.

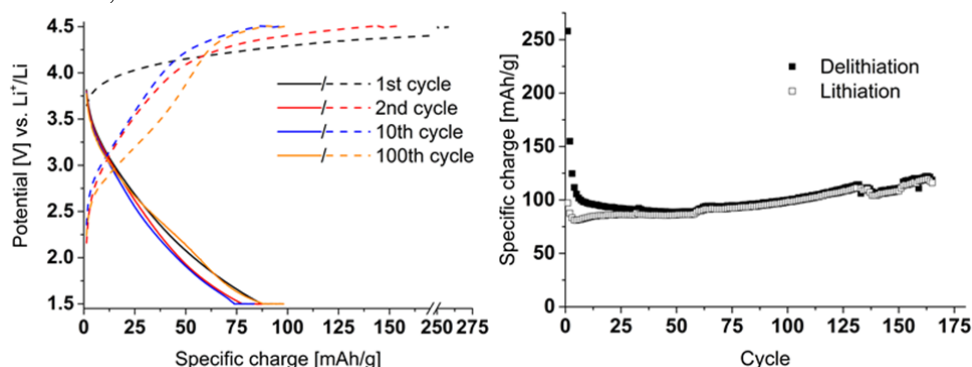


Figure 1 left: Galvanostatic profile of LFMD cycled in a half-cell configuration. After each half-cycle, a 1 h potentiostatic step was implemented. **Right:** The corresponding evolution of the specific charge during cycling of LFMD.

[1] G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, J.-M. Tarascon, J.-M. Angew. Chem. Int. Ed. 46 (2007) 3259-3263.