

Electrochemical and In Situ Investigation of Quaternary Lithium Transition Metal Fluorides in Li-Ion Batteries

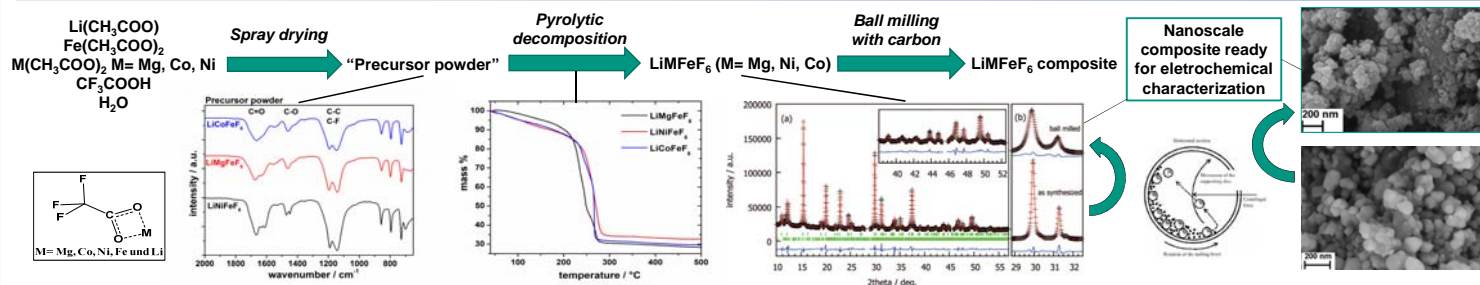
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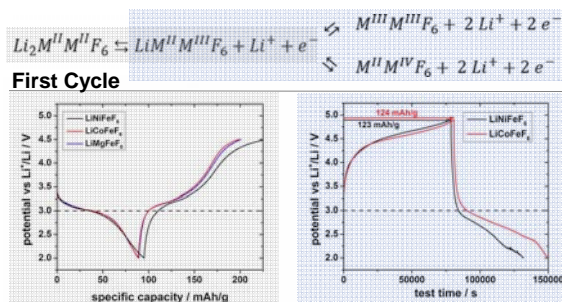
Abstract

Lithium transition metal fluorides are very promising materials compared to common oxide materials with corresponding electrochemically active cations because the more electronegative fluorine atoms increase the redox potential leading to a higher specific energy. However, no reports are given about the electrochemical properties of quaternary lithium transition metal fluorides as positive electrode. In this study, a novel sol-gel route was applied to synthesize several quaternary lithium transition metal fluorides LiMFeF_6 ($M^{2+} = 3d$ transition metal) without the use of toxic chemicals like HF, LiF or F_2 . It is shown that up to 1 eq. lithium can be inserted fully reversible into the LiMFeF_6 host structure with a notable cycling stability and a remarkable rate performance. Furthermore, an in situ x-ray powder diffraction revealed that the host structure is an insertion material. The electrochemical active redox couple $\text{Fe}^{3+/2+}$ was confirmed by Mössbauer analysis.

Synthesis: TFA-Route a Novel Sol-Gel Process for quaternary Lithium Metal Fluorides

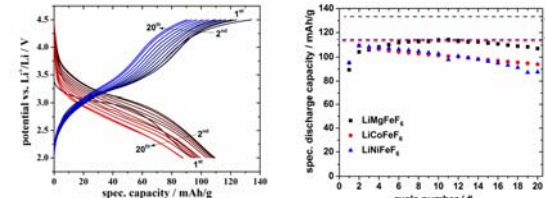


Electrochemical Investigations



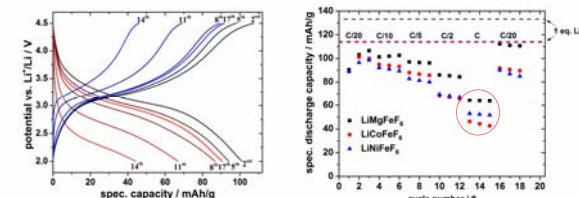
- Close to 1 eq. lithium can be cycled reversible
- No reversible $\text{M}^{3+}/\text{M}^{2+}$ (M = Co, Ni) redox couple

Cycle Stability



- 1 eq. lithium can be cycled reversible (20 cycles)
- Similar capacity fade during cycling ~1 (mAh/g)/cycle

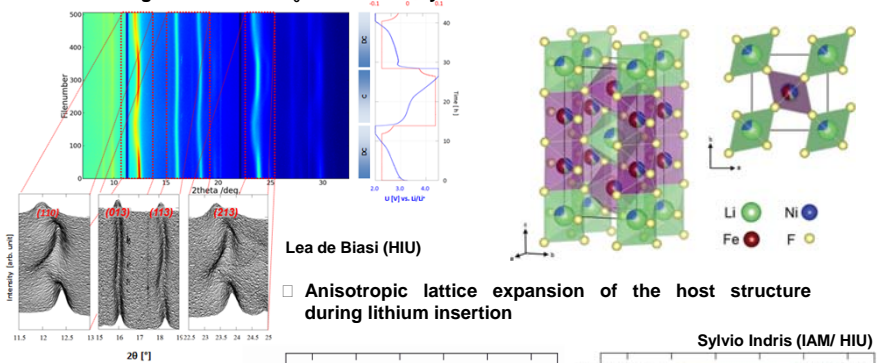
Rate Performance



- Half of the theoretical capacity even at 1 C !

In Situ X-ray Powder Diffraction and Fe Mössbauer Analysis

In situ investigation of LiNiFeF₆ on a laboratory diffractometer



Similar behavior even after 20 cycles

M ²⁺	mAhg ⁻¹	%
Mg	107	80
Co	94	82
Ni	88	77
		±3

Conclusion

- Electrochemical properties of trirutile compounds is unaffected by the divalent cation.
- At a discharge rate of 1 C half of the specific discharge capacity was obtained.
- Anisotropic lattice expansion of the host structure during cycling.
- The $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple was confirmed by Mössbauer analysis.