Karlsruher Institut für Technologie

New synthesis of lithium transition metal fluorides and their use as positive electrode materials in Li-ion batteries

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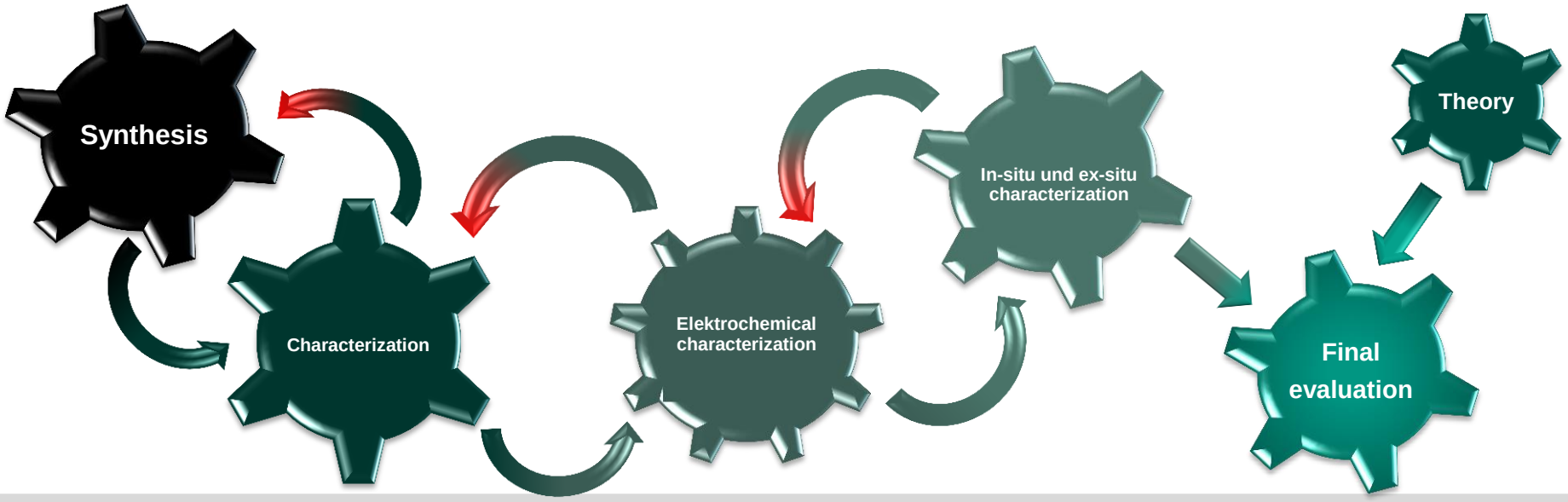


Historical development

- 1972 Watanabe et al.: Patent registration for metal fluorides
  "High Energy Density Battery"
- 1997 Arai et al.
  "Cathode performance and voltage estimation of metal trihalides"

- 2000 Koyama et al. theoretical study about **$LiCaCoF_6$** and **$LiCdCoF_6$**
  "New Fluoride Cathodes for Rechargeable Lithium Batteries"
- 2009 Gocheva et al.
  "Electrochemical Properties of Trirutile **Li_2TiF_6**…"
- 2009 - 2012 **Li_3FeF_6** (4) (Gonzalo et al. Madrid) and **$LiFeFeF_6$** (2)
- 2012 Basa et al.
  "Facile synthesis of **Li_3VF_6**: A new electrochemically active…"

- 2009 - 2012
  At least 7 patents claim for these materials as positive electrodes

Which lithium transition metal fluorides exist?

Li_xMF_y ternary fluorides (e.g. Li_3FeF_6)

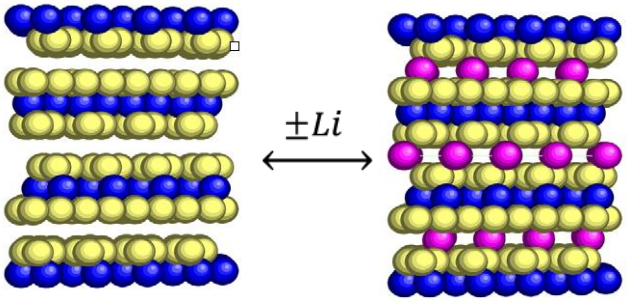
$Li_xM^1M^2F_y$ quarternary fluorides (e.g. $LiCdCoF_6$)

More then 100 compounds are known

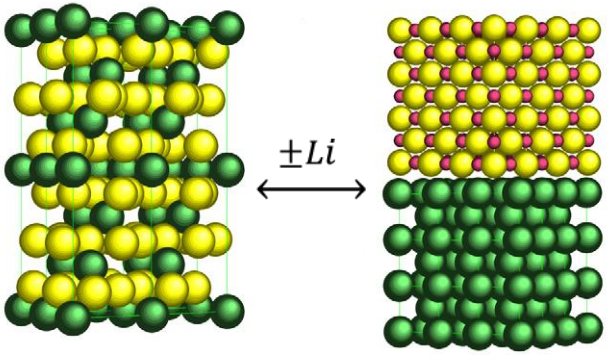
1,0 H 1																	4,0 He 2
6,9 Li 3	9,0 Be 4											10,8 B 5	12,0 C 6	14,0 N 7	16,0 O 8	19,0 F 9	20,2 Ne 10
23,0 Na 11	24,3 Mg 12											27,0 Al 13	28,1 Si 14	31,0 P 15	32,1 S 16	35,5 Cl 17	39,9 Ar 18
39,1 K 19	40,1 Ca 20	45 Sc 21	47,9 Ti 22	50,8 V 23	52 Cr 24	54,9 Mn 25	55,8 Fe 26	58,9 Co 27	58,7 Ni 28	63,5 Cu 29	65,4 Zn 30	69,7 Ga 31	72,6 Ge 32	74,9 As 33	79 Se 34	79,9 Br 35	83,8 Kr 36
85,5 Rb 37	87,6 Sr 38	88,9 Y 39	91,2 Zr 40	92,9 Nb 41	95,9 Mo 42	98 Tc 43	101,1 Ru 44	102,9 Rh 45	106,4 Pd 46	107,9 Ag 47	112,4 Cd 48	114,8 In 49	114,8 Sn 50	121,8 Sb 51	127,6 Te 52	126,9 I 53	131,3 Xe 54
132,9 Cs 55	137,3 Ba 56	138,9 La 57	178,5 Hf 72	180,9 Ta 73	183,8 W 74	186,2 Re 75	190,2 Os 76	192,2 Ir 77	195,1 Pt 78	197,0 Au 79	200,6 Hg 80	204,4 Tl 81	207,2 Pb 82	209,0 Bi 83	209 Po 84	210 At 85	222 Rn 86
223 Fr 87	226 Ra 88	227 Ac 89	261 Rf 104	162 Db 105													

What do we expect for a lithium transition metal fluoride as positive electrode?

Intercalation: „The host structre is retained“



Conversion: „The host structure is rebuild“



	Li_yMO_x	Li_yMF_x
High voltage stable ?	−	+
Electronic conducitivity	+	×
Li ion conductivity	+	−
Flameability	−	+
Cycle stability	+	+
Toxicity	−	?

G. Amatucci, N. Pereira, *Journal of Fluorine Chemistry*, *128,* (**2007**), *243–262*

Synthesis of lithium transition metal fluorides

- **Solid state reaction** **$LiF_{(s)}$** **T** 

$$3\ LiF + FeF_3 \xrightarrow{\Delta} Li_3FeF_6$$

- **Wet chemical** **$HF_{(fl)}$** **T^+ C** 

$$FeCl_3 + 6\ HF + 1.5\ Li_2CO_3 \rightarrow Li_3FeF_6 + 3\ HCl + 1.5\ H_2O + 1.5\ CO_2$$

- **Gas phase fluorination** **$F_{2(g)}$** **T^+ O C** 

$$LiCl + CaF_2 + [Co(NH_3)_6]Cl_3 \xrightarrow{100bar\ F_2 + 500°C} LiCaCoF_6 + \ldots$$

- **High energy ball milling** **$LiF_{(s)}$** **T** 

$$LiF + FeF_2 + FeF_3 \rightarrow LiFeFeF_6$$

TFA – Route: An easy sol-gel process

$Fe(H_3CCOO)_2$
$Li(H_3CCOO)$
F_3CCOOH
H_2O

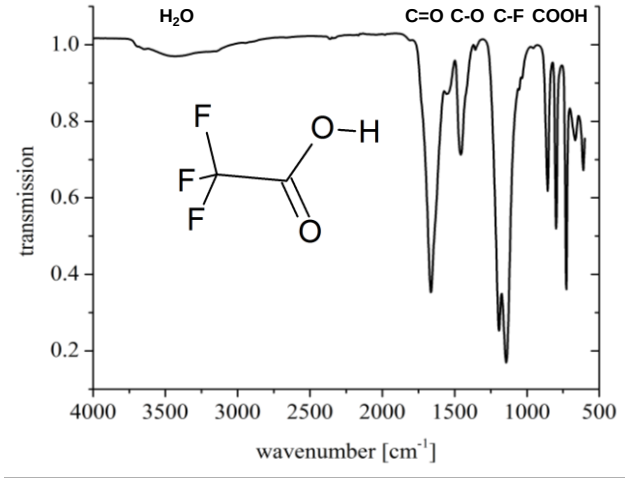
Spray drying

"Precursor Powder"

wet Air → $Fe_2O_3 + 3\ LiF$

dry Air → Li_3FeF_6

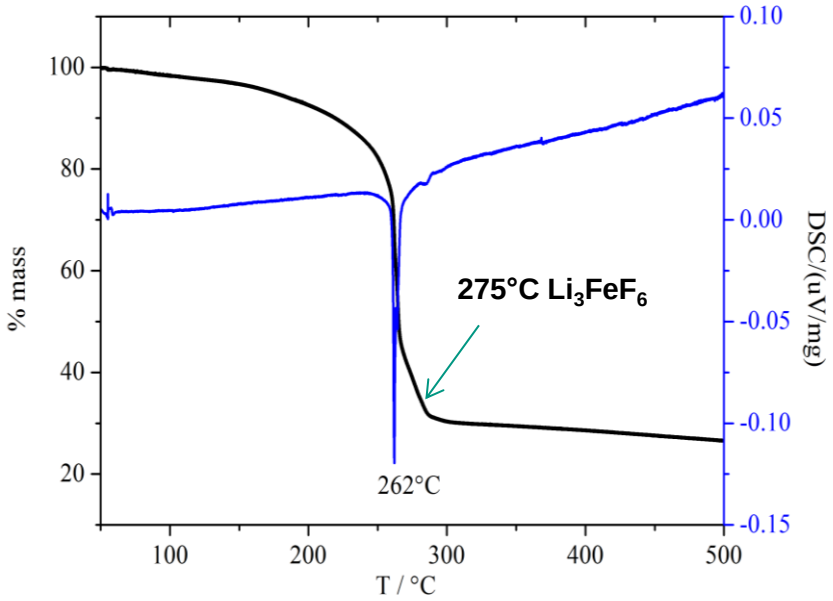
Argon → $FeF_2 + 3\ LiF + coke$



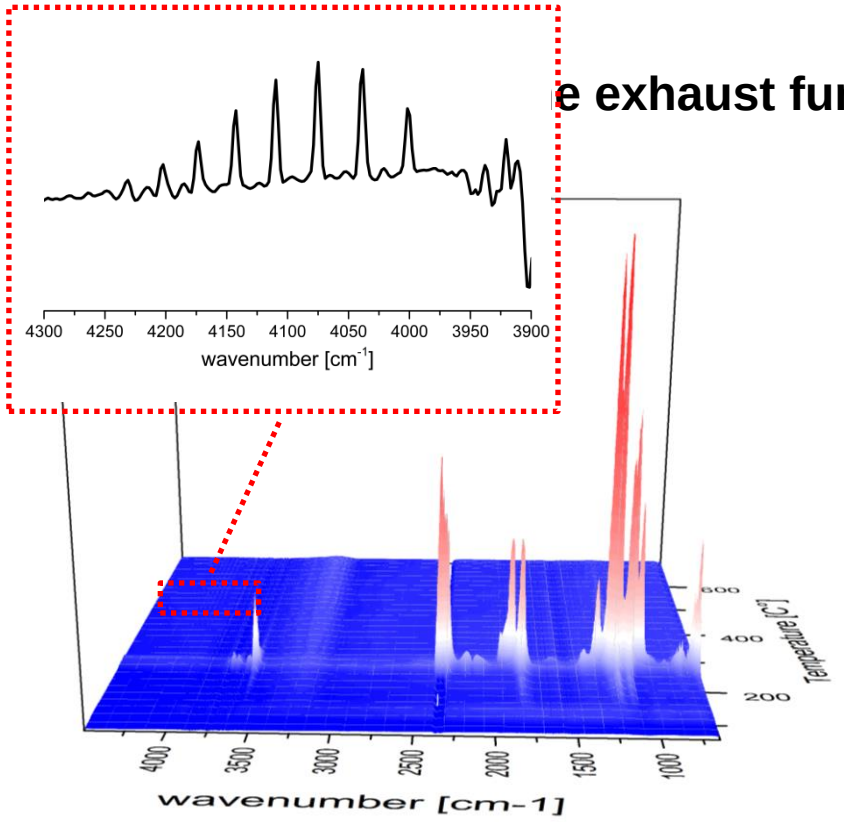
Synthesis can be applied to many lithium transition metal fluorides
e.g. Li_3CrF_6, Li_3VF_6

Pyrolytic decomposition of the precursor

TG-DSC



e exhaust fume

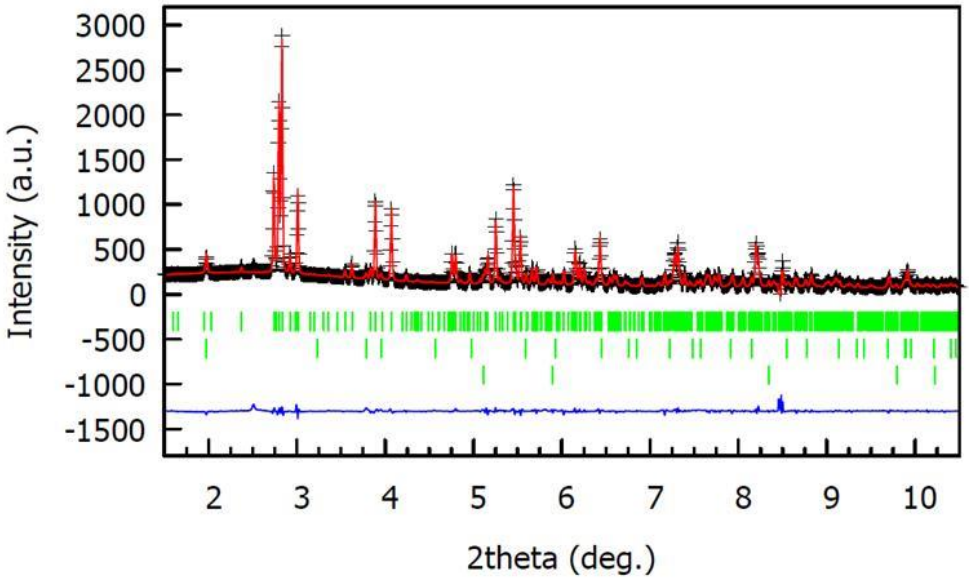


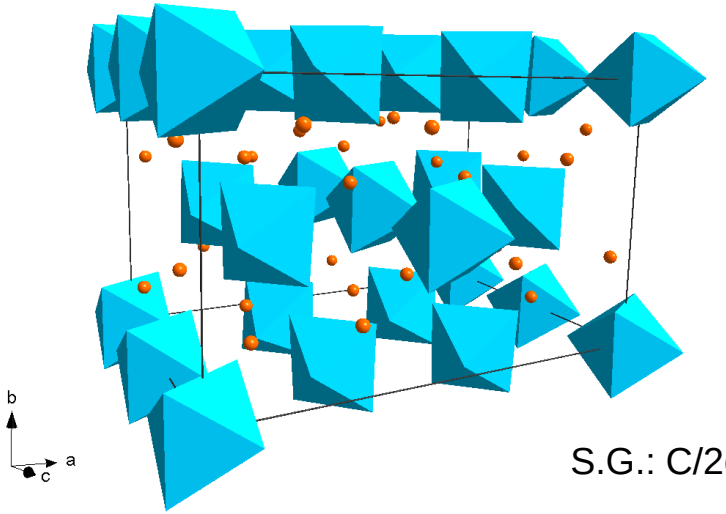
CO_2, CO, CF_3COOH, $(CF_3CO)_2O$ and CF_4 in traces

Formation of HF can be detected at higher temperature

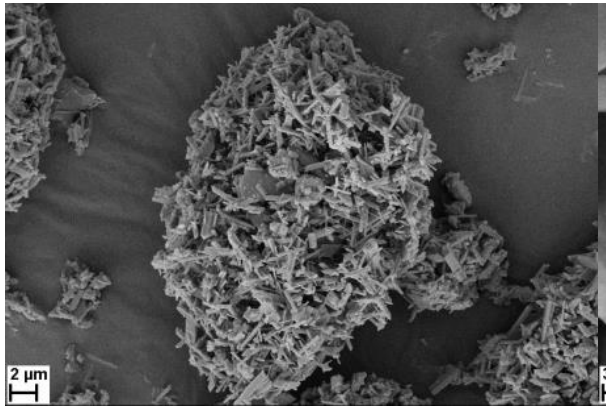
$$7\,Li_3FeF_6 + 11\,H_2O \xrightarrow{\Delta 500°C} LiFe_5O_8 + Fe_2O_3 + 20\,LiF + 22\,HF\uparrow$$

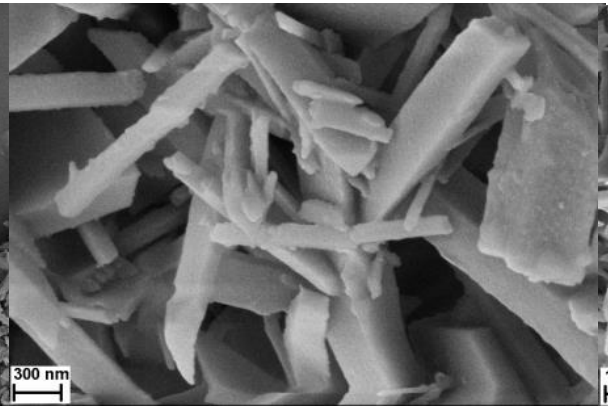
Monoclinic Li_3FeF_6

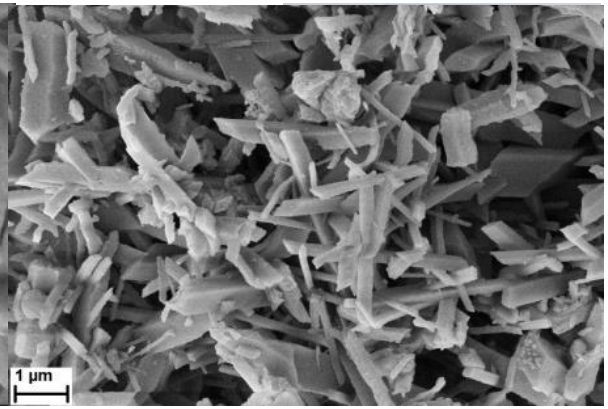




S.G.: C/2c







Preparation of a positive electrode

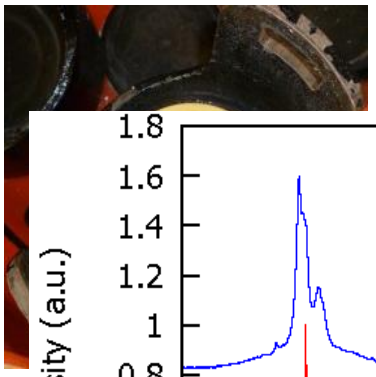
Li_3FeF_6 + C + Binder + NMP (*N*-Methyl-2-pyrrolidon)

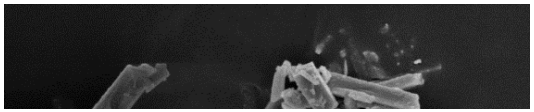
No electrochemical Performance ☹

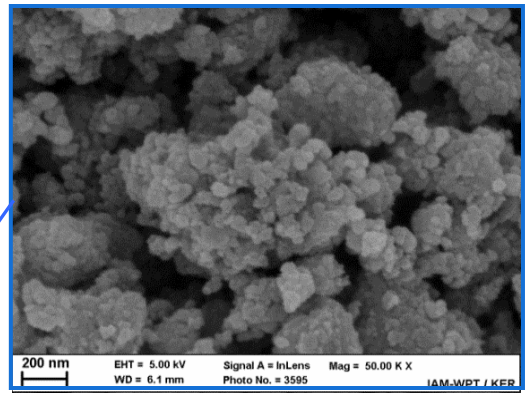
Literature: 1. Small particles (nanoscale)
2. A good contact with a well conductive agent

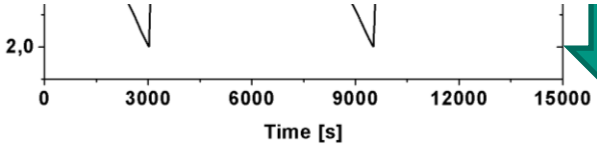
Reduceing the particle size

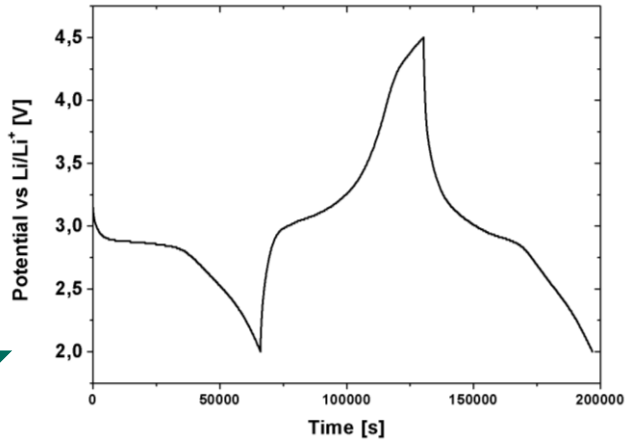
Li_3FeF_6 + C + Binder (72/25/3)











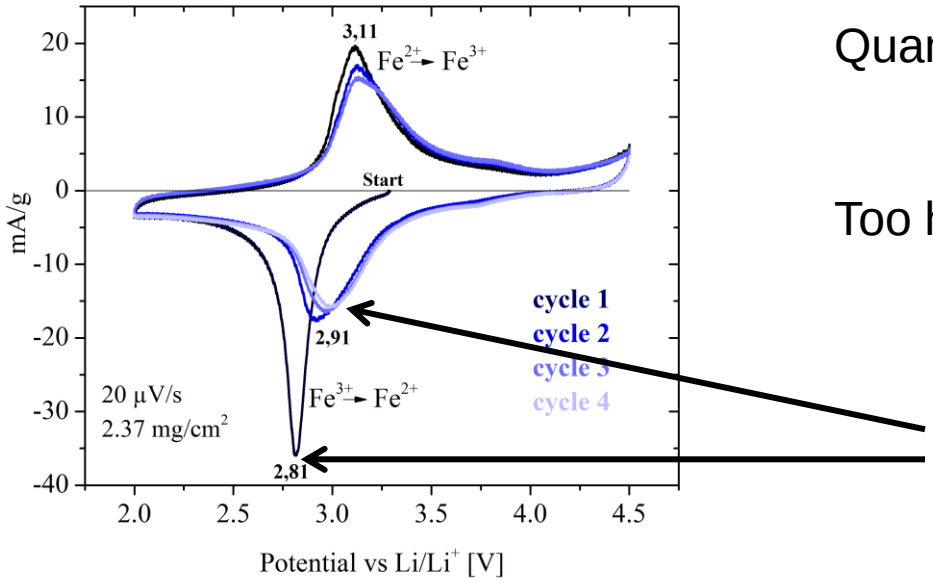
1 eq. Li (140 mAh/g)

7 mAh/g (**5 %**)

128 mAh/g (**91%**)

Which redox couple is involved?

$$Li_2FeF_6 \xleftarrow{-Li\ (charge)} Li_3FeF_6 \xrightarrow{+Li\ (discharge)} Li_4FeF_6$$



Quantum-chemical calculations :

$$Li_3FeF_6 \xrightarrow{-Li} Li_2FeF_6 \qquad > 6\ V\ (1)$$

Too high for common electrolyte systems !

$$Li_3FeF_6 \xrightarrow{+Li} Li_4FeF_6 \qquad 3.0\ V$$

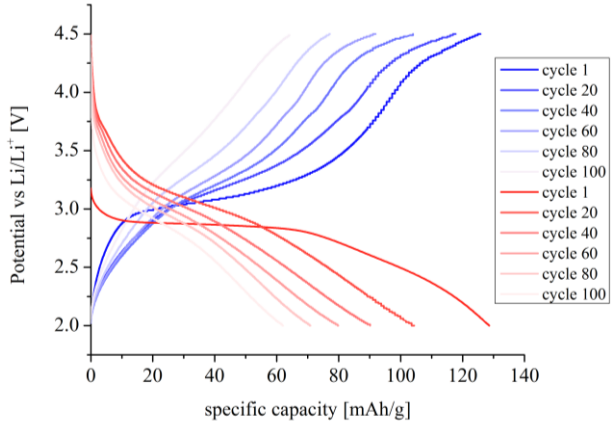
Discharge behavior of the 1st and 2nd cycle is different !

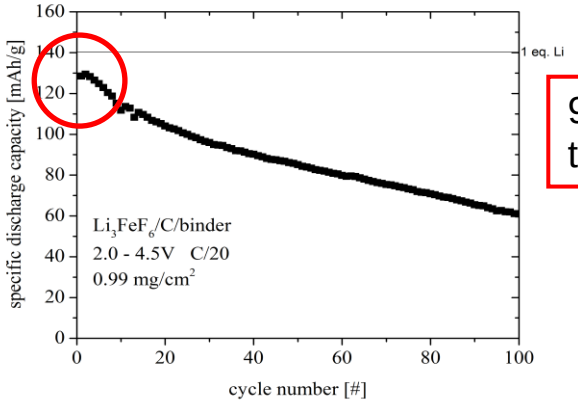
Part of future investigations

(1) J. Kohl et. al, *Journal of Materials Chemistry*, *22,* (**2012**), *15819–15827*

Electrochemcial behavior

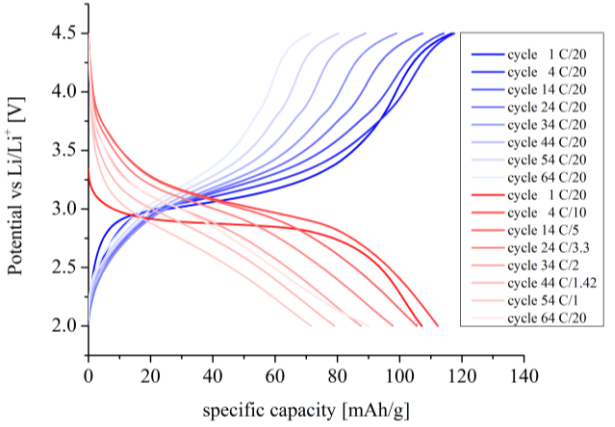
- Long term cycle ability (C/20) (theoretical capacity 140 mAh/g)

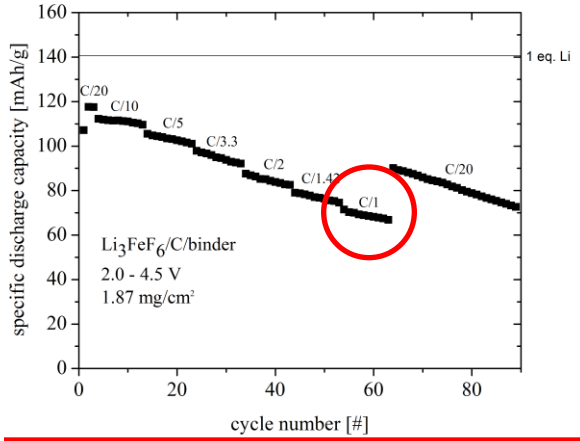




91 % of the theoretical capacity

- Rate performance test

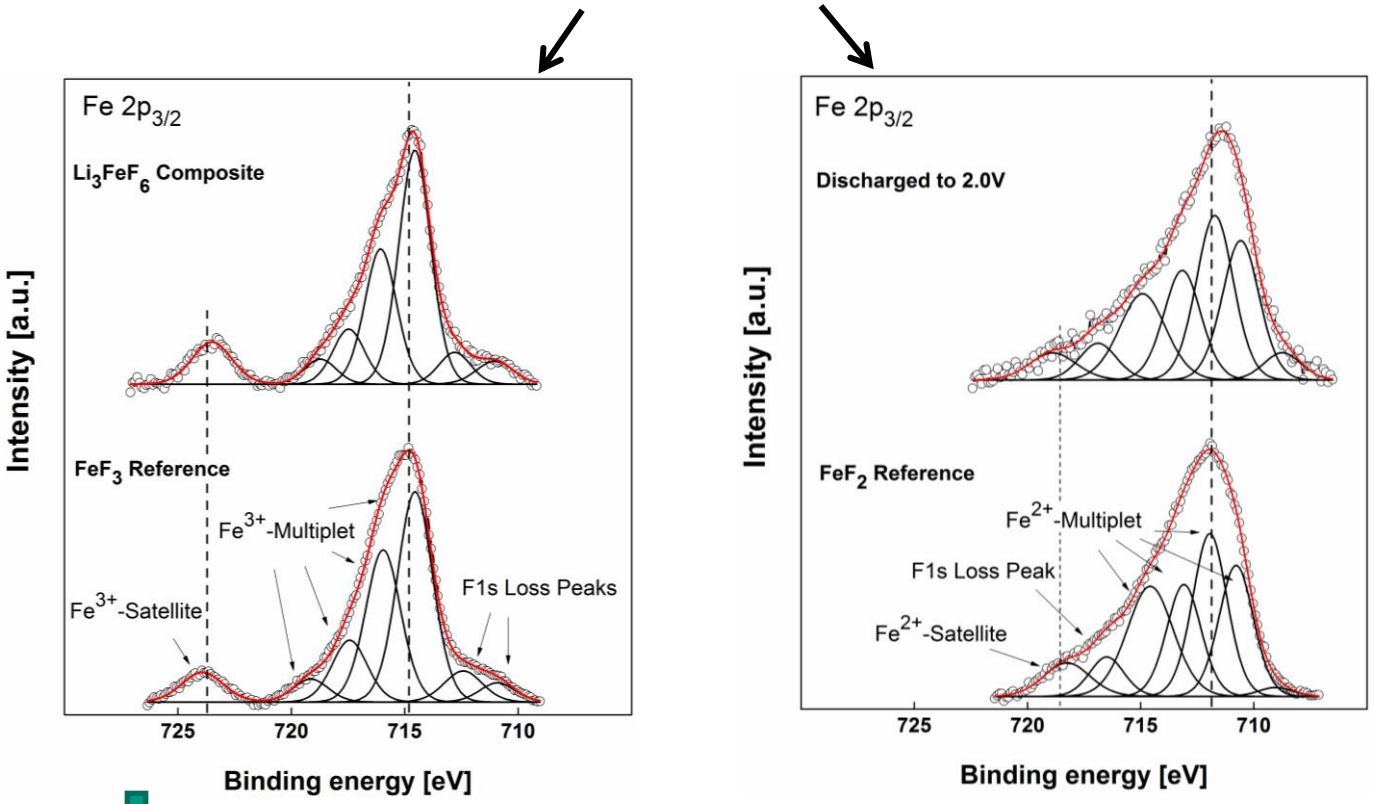




Even at C/1 50% of the theoretical capacity

X-ray photoelectron spectroscopy

$$Li_3FeF_6 \overset{\pm Li}{\longleftrightarrow} Li_4FeF_6$$



The redox couple Fe^{3+}/Fe^{2+} can be confirmed

Summary

- Synthesis of Li_3FeF_6 without high toxic chemicals
- Further processing is required to increase the electrochemcial performance
- Theoretic capacity was nearly reached
- Intercalation and deintercalation of Lithium is reversible
- Even at high discharge rates a good capacity can be obtained

Future work:

- Investigations on new cathode materials e.g. Li_3CrF_6

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HELMHOLTZ GEMEINSCHAFT