Comprehensive Study of the Conversion Reaction Mechanism for CuF₂ as a Cathode Material for Lithium-ion Batteries



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1. Introduction



divalent-3d-transition Among metal fluorides, CuF₂ stands out promising candidate because it has a high specific capacity of 528 mAh/g and the highest theoretical potential of leading an to exceptionally high specific

4. In situ XANES





•2-phase reaction and no Cu(I) • Conversion slows down when the • CuF₂ does not fully convert to Cu

1874 Wh/kg (600 Wh/Kg for LiCoO₂). However, the energy of electrochemical performance of CuF₂ is drastically different in practice. In this project, we place our focus on the investigation of the CuF₂ lithiation mechanism over a full cycle, aiming to gain a fundamental understanding of the whole reaction, and, in particular, the causes for the increase of the overpotential halfway through the 1st discharge and the main factors that which reduce the reversibility of this material.

2. Pristine Material : CCN-CuF₂



5. In situ X-ray Pair Distribution Function

Li 0.3 Li 0.4 Li 0.5 Li 0.6 Li 0.7 Li 0.8

— Li 0.9 —— Li 1.0 —— Li 1.1

Li 1.2 Li 1.3 Li 1.4 Li 1.5 Li 1.6 Li 1.7

PDF on 1st Discharge

Size Evolution

Following Cycling Steps after 1st Discharge: Cu phase dominates all the PDF patterns and CuF₂ shows less and less contribution in the subsequent cycling steps. No or very little CuF₂ forms after the 2nd cycle.



between CuF₂ and C/ZrO₂.



3. Electrochemistry



Redox reactions assignment

1 st Discharge		1 st Charge	
Α	CF _x lithiation	B ₁ '	Cu(0) to Cu(I) oxidation
В	CuF ₂ one-step lithiation	B ₂ ′	Cu(I) to Cu(II) / Cu(0) to Cu(II
B'	reaction of hydrated CuF ₂ phase	C'	oxidation of SEI formed in C
С	electrolyte decomposition	D'	oxidation of SEI formed in D
D	electrolyte decomposition	Ε'	reaction related to carbon

Acknowledgement and References

1st Discharge

Phase Fraction

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

large-Cu small-Cu CuF₂

- $CuF_2 \rightarrow Cu$ 2-phase reaction and it gradually slows down.
- Small Cu particle stops growing at about Li =
- 1.0.
- There is some CuF₂ remaining at the end of discharge.

6. Ex situ Solid-state NMR



1st Discharge

• LiF starts to form right in the beginning.

• The negative shift of the chemical shift from process A to B suggests different lithiation process leading to a different local environment for LiF. (A: $CF_x \rightarrow C + LiF$; B: $CuF_2 \rightarrow Cu + 2LiF$)

• LiF particle starts to grow bigger when capacity reaches about Li=1.0 (suggested by T_1).





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but the size remains small.

• Li₂PO₃F (-78 ppm) is observed at the end of charge.





The growth of Cu phase occurs in the beginning of the CuF₂ conversion, which enhances the electronic conductivity and helps compensate for the insulating effect from the LiF phase. Cu is soon covered by an insulating LiF layer, thus the electronic conductivity decreases leading to a larger overpotential. In addition, SEI formation on the Cu surface enlarges the overpotential even more, consequently, a continuous potential reduction is observed on discharge. The charging mechanism for CuF₂ is fundamentally different from most of the other conversion materials. Cu dissolves in the electrolyte and consumes the LiF thereby hindering the Cu to CuF₂ transformation. In order to prevent the dissolution from taking place and make this material more practical for applications, approaches such as surface coating or electrolyte substitution can be employed to stabilize Cu metal at high potentials.