

$\text{Cu}_x\text{Fe}_{1-x}\text{F}_2$ solid solution as cathode material for Li ion battery

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Transition metal fluorides are potential candidates for advanced Li ion battery cathodes due to their high specific capacities and high reaction potentials.[1,2] High reversibility has been achieved in some conversion compounds, but for their use in commercial batteries there are still energy-efficiency related issues due to the big polarization and hysteresis. Further improvements require better understanding the conversion reaction mechanisms and origins of the polarization and the hysteresis.

The metal fluorides, FeF_2 and CuF_2 both react with Li via a direct conversion process (without intercalation step), but have much different electrochemical behaviors, which may be due to the different diffusivity of the cations (*i.e.*, Fe^{2+} vs. Cu^{2+}).[2] In this study, we investigated binary CuF_2 - FeF_2 system to see how the transition metal ions affect the electrochemistry. We were able to synthesize $\text{Cu}_x\text{Fe}_{1-x}\text{F}_2$ solid solution from CuF_2 - FeF_2 mixture. As shown in Fig. 1, $\text{Cu}_x\text{Fe}_{1-x}\text{F}_2$ has isostructure to FeF_2 , forming tetragonal rutile structure according to the synchrotron X-ray diffraction patterns. CuF_2 possesses monoclinic structure, which may also be taken as a distorted rutile structure, due to the strong Jahn-Teller distortion of Cu^{2+} ion. Cu appears to be stabilized in the rutile framework by forming the solid solution.

In comparison to CuF_2 , FeF_2 and simple CuF_2 - FeF_2 mixture, $\text{Cu}_{0.5}\text{Fe}_{0.5}\text{F}_2$ solid solution shows different electrochemical behavior. As shown in Fig. 2, the voltage plateau of Cu in CuF_2 and Fe in FeF_2 was approximately 2.9 V and 1.7 V, respectively, which is comparable to previous study[2]. The plateau of each transition metal in CuF_2 - FeF_2 mixture was almost identical to pure CuF_2 and FeF_2 . However, it is noteworthy that the voltage plateau of Cu was slightly decreased (~ 2.7 V) and that of Fe was remarkably increased (~ 2.3 V) after forming the solid solution. Currently it is not clear that the voltage change is due to the change in intrinsic redox potential of Cu and Fe or due to the kinetic effect.

Detailed analysis on local structure and their evolution with lithiation is under progress by using transmission electron microscopy, in-situ X-ray diffraction, and X-ray absorption spectroscopy, and will be discussed in the meeting.

References

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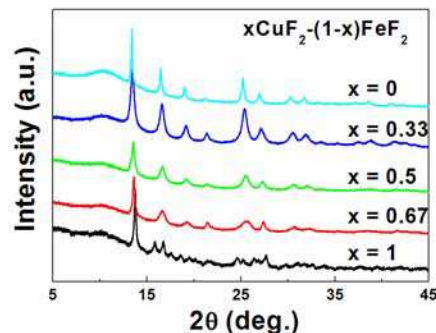


Figure 1. X-ray diffraction patterns of $\text{Cu}_x\text{Fe}_{1-x}\text{F}_2$ ($x = 0, 0.33, 0.67, 1$).

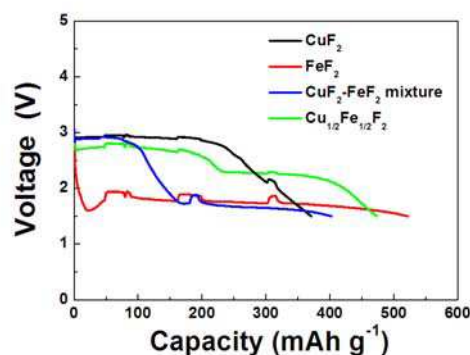


Figure 2. Initial discharge profiles of CuF_2 (black), FeF_2 (red), CuF_2 - FeF_2 mixture (blue) and $\text{Cu}_{0.5}\text{Fe}_{0.5}\text{F}_2$ solid solution (green).