

## Enhancing the Cathode Functionality of Glycol Synthesized $\text{LiFeSO}_4\text{F}$ by Controlling the Surface Chemistry

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Recently, the *tavorite* polymorph of  $\text{LiFeSO}_4\text{F}$  has attracted considerable attention within the lithium battery community stimulated by the high potential for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple (3.6 V vs.  $\text{Li}/\text{Li}^+$ ), competitive specific capacity (151 mAh/g), beneficial structure for fast lithium ion transport, and low temperature synthesis<sup>1</sup>. It is thus considered as an attractive contender to  $\text{LiFePO}_4$  as a next-generation cathode material. Since its discovery, various synthesis routes for producing *tavorite*  $\text{LiFeSO}_4\text{F}$  have been explored, including ionothermal<sup>1</sup>, solvothermal<sup>2</sup>, polymer assisted<sup>3</sup>, and solid-state methods<sup>4</sup>. Reviewing the literature, one can conclude that the electrochemical performance presented for this material has been notably varied. This inconsistency is difficult to understand given the excellent purity, crystallinity, and similar sample morphologies achieved in most cases.

In this contribution, we examine the role of the surface chemistry on the electrochemical performance of *tavorite*  $\text{LiFeSO}_4\text{F}$ . We demonstrate that particularly restricted performance may be obtained for materials synthesized using tetraethylene glycol (TEG) as reaction media. While the limited performance of materials prepared in TEG is a substantial drawback, the use of this solvent as a reaction media should still be pursued as it presents one of the most economical synthesis routes. Therefore, understanding the limitations of the materials synthesized in TEG, and developing strategies to negate these drawbacks, is extremely interesting. This is driven by both a fundamental need to explain the differences in performance for phase pure materials synthesized in different solvents, and to develop a commercially practical and scalable synthesis of high performing *tavorite*  $\text{LiFeSO}_4\text{F}$ .

By careful surface characterization, we show that the restricted performance of  $\text{LiFeSO}_4\text{F}$  prepared in TEG can be largely attributed to residual solvent traces remaining on the surface of pristine powders, inhibit the electrochemical reactions. Moreover, we show that the cycling performance of  $\text{LiFeSO}_4\text{F}$  can be significantly improved by removing the TEG residues and applying a conducting polymer coating, which decreases the contact resistance between the electrode components and creates a highly percolating network for electron transport throughout the composite material (Figure 1). This surface modified material displays a well defined voltage plateau with sharp and distinct charge and discharge end points, as expected from a two-phase lithium insertion compound.

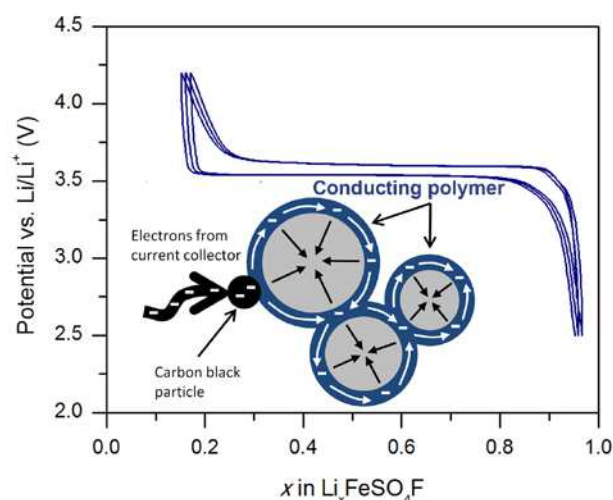


Figure 1. Galvanostatic cycling of the  $\text{LiFeSO}_4\text{F}$  composite material at a rate of  $C/20$ . The inset shows a schematic illustration explaining the suggested mechanism of performance improvement by surface confined facilitated electron transport, leading to improved electron distribution in the active material particles.

### References

- (1) N. Recham, J.-N. Chotard, L. Dupont, C. Delacourt, W. Walker, M. Armand, J.-M. Tarascon, *Nat. Mater.* **68–74**, 9, (2010).
- (2) R. Tripathi, T. N. Ramesh, B. L. Ellis, L. F. Nazar, *Angew. Chem.* **8920–8924**, 122, (2010).
- (3) M. Ati, W. T. Walker, K. Djellab, M. Armand, N. Recham, J.-M. Tarascon, *Electrochem. Solid-State Lett.* **A150–A153**, 13, (2010).
- (4) M. Ati, M. T. Sougrati, N. Recham, P. Barpanda, J.-B. Leriche, M. Courty, M. Armand, J.-C. Jumas, J.-M. Tarascon, *J. Electrochem. Soc.* **A1007–A1015**, 157, (2010).