Structural, Electrochemical and Magnetic Properties of a Novel $KFeSO_4F$ Polymorph

Laura Lander[a,b], GwenaëlleRousse[a,b,c], Artem M. Abakumov[d], Moulay-TaharSougrati[e], Gustaaf Van Tendeloo[d], Jean-Marie Tarascon[a,b,c]

[a]*Chimie du Solide et Energie, Collège de France, 11 Place Marcelin Berthelot, 75005 Paris, France*
[b]*Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[c]*Sorbonne Universités - UPMC Univ Paris 06, 4 Place Jussieu, 75005 Paris, France.*
[d]*EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[e]*ICGM Institut Charles Gerhardt - Université Montpellier, Place Eugène Bataillon, 34095 Montpellier, France*

email address of the presenting author: laura.lander@college-de-france.fr

Since the discovery of the promising electrode material $LiFePO_4$, recent research has been focusing on the development of new iron-based polyanionic materials for next generations Li- and Na-ion batteries displaying better performances while still preserving cost and sustainability benefits.[1,2] On this quest, our group explored the wide family of sulfate-based compounds, where the most prominent members are monoclinic $Li_2Fe(SO_4)_2$ showing a potential of 3.83 V vs Li^+/Li^0 and $LiFeSO_4F$ crystallizing either in a *tavorite* or *triplite* crystal structure with the latter presenting a potential of 3.9 V vs Li^+/Li^0 .[3,4]

In order to further investigate the rich crystal chemistry offered by 3d-metal-basedfluorosulfates, we studied the effect of the replacement of Li by other alkali metals such as Na and K. One of the so discovered phases was $KFeSO_4F$, which crystallizes in the orthorhombic $Pna2_1$ space group and from which K^+ ions can be extracted in a complex electrochemical process.[5]

Knowing that sulfate-based compounds are prone to polymorphism, we recently unveiled a new low-temperature $KFeSO_4F$ polymorph.[6]Using combined synchrotron and neutron powder diffraction as well as electron diffraction, it was shown that the compound adopts a complex layered-like structure that crystallizes in a large monoclinic unit cell. Impedancemeasurements together with the Bond Valence Energy Landscape approachshow that the K^+ ions, which are located between the layers, are mobile within the structure and are electrochemically removed at an average potential of 3.7 V vs. Li^+/Li^0. Lastly, neutron diffraction experiments coupled with SQUID measurements reveal a long range antiferromagnetic ordering of the Fe^{2+} magnetic moments.These results confirm once more the richness of polymorphisms in sulfate-based materials and we hereby want to encourage the further exploration of their interesting electrochemical and physical properties.

[1] Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Goodenough, J. B. J. Electrochem. Soc.144 (1997)2581–2586.
[2] Masquelier, C.; Croguennec, L. Chem. Rev.113 (2013) 6552–6591.
[3] Reynaud, M.; Ati, M.; Melot, B. C.; Sougrati, M. T.; Rousse, G.; Chotard, J.-N.; Tarascon, J.-M. Electrochem. Commun.21 (2012) 77–80.
[4] Ati, M.; Melot, B. C.; Chotard, J.-N.; Rousse, G.; Reynaud, M.; Tarascon, J.-M. Electrochem. Commun.13 (2011) 1280–1283.
[5] Recham, N.; Rousse, G.; Sougrati, M. T.; Chotard, J.-N.; Frayret, C.; Sathiya, M.; Melot, B. C.; Jumas, J.-C.; Tarascon, J.-M. Chem. Mater.24 (2012)4363-4370.
[6] Lander, L.; Rousse, G.; Abakumov, A. M.; Sougrati, M.; van Tendeloo, G.; Tarascon, J.-M. J Mater Chem A(2015) Advanced Paper.