

Structure and Electrochemistry of Carbon-Metal Fluoride Nanocomposites Fabricated by a Solid State Redox Conversion Reaction Utilizing CF

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The fundamental route to attaining the highest specific capacity of an electrode is to utilize all of the possible oxidation states of the electrode material during the redox cycle. Intercalation processes limit the degree of transition metal reduction possible due to limited number of vacancies available for Li intercalation. As opposed to such intercalation reactions, the reversible conversion process enables the full redox utilization of the transition metal through the following reaction:

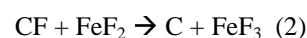


Previously, such reversible conversion reactions were limited to low potential materials suitable for use as negative electrodes. This was first demonstrated by Tarascon's group for the oxide and sulfide chalcogenides¹ and later by our group for the transition metal nitrides². Recently our group has demonstrated the application of reversible conversion to high voltage (>2V) positive electrodes with appreciable energy density. This was made possible by utilizing compounds with highly ionic bonding such as metal fluorides to raise the conversion reaction potential of (1) by at least 1 V to the 2-3V range. This enabled exceptionally high reversible specific capacities approaching 700 mAh/g at energy densities exceeding 1200 Wh/kg.^{3,4,5} In a parallel effort, Li et al. has also shown reversible metal fluoride conversion in lower voltage TiF₃ and VF₃ metal fluorides⁶. These compounds exhibited good room temperature reversibility.

Many of the higher voltage metal fluorides were found to have limited electrochemical activity with lithium due to their electrically insulative nature brought about by a characteristically large band gap. Our group has recently introduced the use of carbon metal fluoride nanocomposites (CMFNCs) to enable the electrochemical activity of higher voltage metal fluorides^{3,4,5}. The use of nano sized (20nm) crystallites reduces the electron path length and also creates a highly active, defect rich surface. The nanocrystallites are embedded in a conductive carbon matrix to enable interparticle electronic conductivity significantly. Besides drastically improving the known intercalation reaction efficiency occurring at approximately 3V⁴, the CMFNCs also enabled a reversible conversion process resulting in specific capacities and energy densities 4X and 2X that of LiCoO₂, respectively⁵. We have shown extension of this system from FeF₃ to other metal fluorides: FeF₂, NiF₂ and CoF₂. It has also been demonstrated one can evolve from the use of C as the conductive matrix to highly conducting oxide matrices such as VO_x. In addition, we have shown it is entirely possible to enable high performance electrodes from the use of a nanocomposite of LiF and Me.³ Such electrodes are of fundamentally lower cost and enable the use of such technology in Li-ion batteries.

Initial fabrication of CMFNCs were accomplished by the use of high energy mechanical milling of the desired components in order to demonstrate the viability of the concept. In order to develop a more elegant, homogenous, technique on the laboratory scale and identify a facile route to solid solution synthesis, we aimed to introduce a CMFNC fabricated by through a chemical synthesis where the respective components are formed in-situ via reactive precursors.

Herein we introduce a solid state redox driven conversion process for CMFNCs through reactive high energy milling. We utilize carbon fluoride as an oxidizing agent for FeF₂ through high energy mechanomilling, thereby creating an intimate conductive nanocomposite of FeF₃ and C from insulating CF₁ and FeF₂ precursors according to the following reaction:



All reactions were characterized by both x-ray diffraction and Fourier transform infrared spectroscopy. FTIR will be shown to provide excellent insight to the progression of the CF and C phases and the metal fluoride during the course of the reaction. Such nanocomposites resulted in a 4 order of magnitude increase in electrical conductivity and enabled excellent specific capacity approaching 500 mAh/g vs Li with good reversibility, although at slow rates. Utilizing the theoretical basis of the technique, other couples were examined to experimentally isolate the oxidative power of CF₁. In the process we have also shown a composite of CF₁:CrF₂ can be easily converted to C:CrF₃. The resulting nanocomposite exhibited a specific capacity of 682 mAh/g at an average voltage of approximately 1.9V.

The technique will also be shown to be a powerful method for the fabrication of single phase metal fluoride solid solutions as demonstrated with the fabrication of Cr_{0.5}Fe_{0.5}F₃.

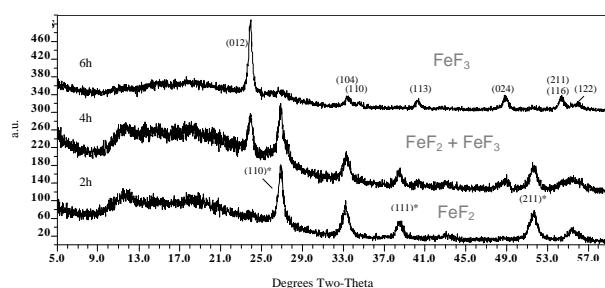


Fig. 1 XRD patterns of FeF₂:CF₁ mixtures high energy milled for 2, 4, and 6h hours showing the development of FeF₃. (hkl)* denote peaks associated to FeF₂, (hkl) are for FeF₃.

References

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