Direct Fluorination of Iron (II, III) Oxide Conversion Electrodes

Hui Zhou, Jagjit Nanda, Surendra K. Martha, Juan Carlos Idrobo, Loïc Baggetto, Gabriel M. Veith, Sheng Dai, Sreekanth Pannala, Nancy J. Dudney
Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
Jamie Adcock
Department of Chemistry, University of Tennessee, Knoxville, TN 37996 USA

Multivalent conversion-based transition metal (TM) compounds have significantly higher specific capacity due to their multiple red-ox states contributing towards transfer of > 1 lithium per transition metal atom. 1-2 Iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$) are examples of such high capacity conversion electrodes having other advantages such as low cost, natural abundance and environmental benignity. 3 A relatively lower redox potential with respect to Li/Li$^+$ makes them more suitable as anodes for lithium batteries. 4 On the other hand, their fluoride counterparts such as FeF$_3$ have higher redox potential, and capacity contribution derived from intercalation and conversion mechanisms. The major drawback of iron fluoride is their poor electronic conductivity due to the higher ionicity of the Fe-F bonds. 5 One of the approaches for overcoming this barrier is developing synthesis methods for converting fluorides to oxyfluorides. 6 In this work, we demonstrate a novel approach where we use a direct fluorination method to convert iron oxides to oxyfluoride using a fluidized bed reactor.

Fluorination of nano-Fe$_3$O$_4$ (n-Fe$_3$O$_4$) powder was carried out using a fluidized bed reactor by controlling F$_2$ partial pressure and reaction temperature (T). XPS study confirmed that with increase in fluorination temperatures, more F was introduced into Fe$_3$O$_4$ with concomitant reduction of surface oxygen species, especially for T > 100 °C (Figure 1).

X-ray diffraction data (not shown here) of fluorinated Fe$_3$O$_4$ showed only a slight shift in lattice parameters upon fluorination. Electron Energy Loss Spectroscopy (EELS) experiments showed a weak F signal for sample fluorinated at > 120 °C. These evidences suggest the fluorination occur only at the surface of n-Fe$_3$O$_4$.

Electrochemical study of fluorinated n-Fe$_3$O$_4$ showed increased intercalation capacity and raised intercalation potential after fluorination, compared to the pristine n-Fe$_3$O$_4$ (as shown in Figure 2). Such enhancement could be ascribed to the possible formation of oxyfluoride on the surface. The plausible reaction mechanism would be also discussed.

Acknowledgement
This research is sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Electron microscopy work is supported Oak Ridge National Laboratory's SHaRE User Facility funded by Office of Basic Energy Sciences, DOE.

References: