

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

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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_2O_3 and Fe_3O_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_3O_4 (n- Fe_3O_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_3O_4 with concomitant reduction of surface oxygen species, especially for $T > 100^\circ\text{C}$ (Figure 1).

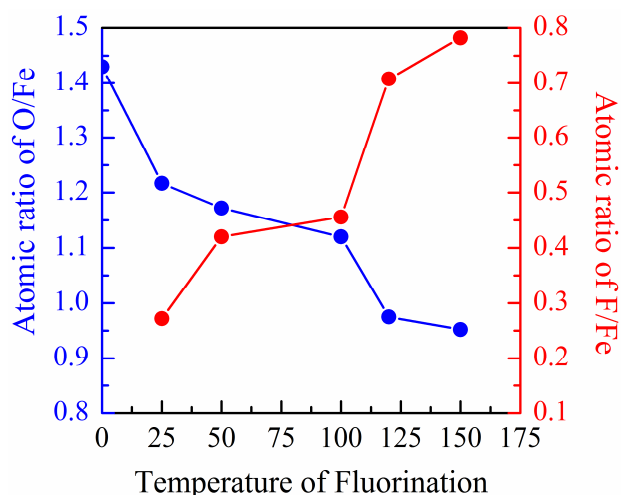


Figure 1. Change in the ratio of O/Fe and F/Fe with increased fluorination temperatures, which were calculated on the XPS data of O 1s, F 1s and Fe 3p peaks.

X-ray diffraction data (not shown here) of fluorinated Fe_3O_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 $> 120^\circ\text{C}$. These evidences suggest the fluorination occur only at the surface of n- Fe_3O_4 .⁷

Electrochemical study of fluorinated n- Fe_3O_4 showed increased intercalation capacity and raised intercalation potential after fluorination, compared to the pristine n- Fe_3O_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.

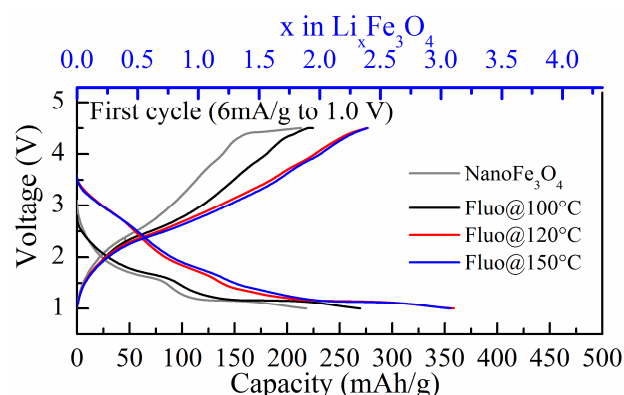


Figure 2. 1st cycle charge-discharge profile of n- Fe_3O_4 and those fluorinated at 100, 120 and 150 $^\circ\text{C}$ cycled between 4.5 and 1.0 V with the current density of 6 mA/g.

Acknowledgement

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