

# Insight into the charging-discharging of magnetite electrodes: *In-situ* XAS study

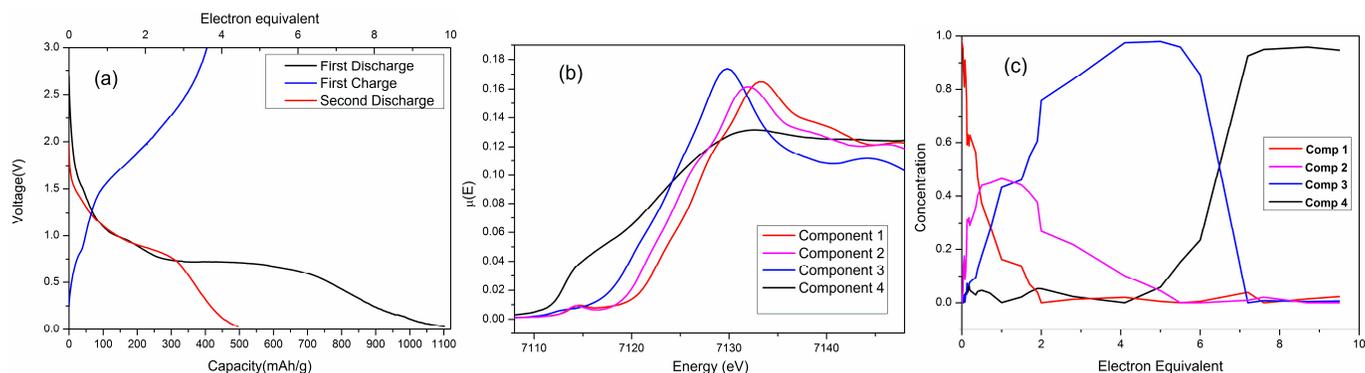
C. Nayak, Abharana N., S. N. Jha and D. Bhattacharyya

Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA.

nayakc@barc.gov.in

Magnetite ( $\text{Fe}_3\text{O}_4$ ) has emerged as a promising electrode material in rechargeable batteries because of its natural abundance, low cost, low toxicity and high specific capacities.  $\text{Fe}_3\text{O}_4$  exhibits both intercalation and conversion mechanism and it involves 8 Li ions during its reduction. The multi electron transfer enables higher energy density of these electrodes compared to purely intercalation electrodes. However, it suffers from high hysteresis and high capacity loss with cycling. The reasons for the capacity fading in conversion electrodes are still not very clear and lot of research is going on with an aim to design a high capacity electrode with performance stability over a large number of cycles. *In-situ*/operando research in the area of batteries has gain popularity in recent past as it can give valuable information regarding changes taking place in the electrode materials during the charging-discharging of the batteries and thus can address various problems associated with battery performance [1,2].

In the present work we have used operando XAS to understand the structural changes around Fe cations during the charging-discharging of the  $\text{Fe}_3\text{O}_4$  electrodes in Li ion battery. Fig 1(a) shows the voltage profile of  $\text{Fe}_3\text{O}_4$  electrodes during galvanostatic cycling at the rate of  $53\text{mA g}^{-1}$  in the voltage range of 0.03-3V. The XANES data recorded during the first discharge was analysed using chemometric techniques like Principal Component Analysis (PCA) and Multivariate Curve Resolution- Alternate Least Square (MCR-ALS). Figure 1 (b) & (c) show the components and their concentration profile obtained from the MCR-ALS analysis of the XANES data recorded during the first discharge of  $\text{Fe}_3\text{O}_4$  electrode in Li ion battery.



**Figure 1.** (a) Voltage profile of  $\text{Fe}_3\text{O}_4$  electrode during galvanostatic cycling (b) XANES spectra of the MCR-ALS components during first discharge of  $\text{Fe}_3\text{O}_4$  electrode (c) Concentration profile of the MCR-ALS components first discharge of  $\text{Fe}_3\text{O}_4$  electrode

The components of the MCR-ALS analysis during the first discharge of  $\text{Fe}_3\text{O}_4$  electrode have been identified respectively as  $\text{Fe}_3\text{O}_4$ ,  $\text{Li}_x\text{Fe}_3\text{O}_4$ , FeO and metallic Fe. The EXAFS analysis shows that the fraction of tetrahedral Fe cations decreases and after 0.4 electron equivalent Fe cations exists in octahedral coordination environment only. Therefore, from the operando XANES and EXAFS analysis, it becomes evident that the lithiation of magnetite during the first discharge is a multi-step process, where Li insertion in the  $\text{Fe}_3\text{O}_4$  structure results in migration of Fe cations in the tetrahedral 8a site to octahedral sites (16c or 16d) and finally formation of  $\text{Li}_x\text{Fe}_3\text{O}_4$  where all Fe cations exist in octahedral coordination. The next step is conversion of  $\text{Li}_x\text{Fe}_3\text{O}_4$  phase into the rocksalt FeO phase, which finally converts to metallic Fe phase. From Fig. 1(c) it can also be seen that the intercalation of  $\text{Fe}_3\text{O}_4$  which results in formation of  $\text{Li}_x\text{Fe}_3\text{O}_4$ , overlaps with the conversion reaction of  $\text{Li}_x\text{Fe}_3\text{O}_4$  to FeO. Further XANES and EXAFS analysis of the first charge and second discharge of  $\text{Fe}_3\text{O}_4$  electrodes show that the completely lithiated electrode material never returns to  $\text{Fe}_3\text{O}_4$  phase on charging, instead the subsequent cycles after the first discharge are due to the conversion reaction between FeO and metallic Fe. In conclusion, this study gives a detailed structural analysis of the  $\text{Fe}_3\text{O}_4$  electrodes in Li ion battery during charging-discharging cycles.

[1] Huie, M. M., Bock, D. C., Wang, L., Marschilok, A. C., Takeuchi, K. J. & Takeuchi, E. S. (2018) *J. Phys. Chem. C* **122**, 10316.

[2] Zhang, W., Bock, D. C., Pelliccione, C. J., Li, Y., Wu, L., Zhu, Y., Marschilok, A. C., Takeuchi, E. S., Takeuchi, K. J. & Wang, F. (2016) *Adv. Energy Mater.* **6**, 1502471.

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