

Suppression of Spatial Inhomogeneity of Electrode Reaction for Lithium Iron Phosphate by Carbon Nanotube Decoration

Tatsuya Oi¹, Tomohiro Osaki¹, Hirona Yamagishi², Yusaku Yamamoto¹,
Misaki Katayama², and Yasuhiro Inada¹

1) Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

2) The SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

The electron conductivity of the active material for lithium ion battery is an important parameter to improve its performance. The poor conductivity of LiFePO₄ (LFP) causes an inhomogeneous progress of the electrode reaction in the cathode plane [1]. Carbon nanotubes (CNTs) are effective to gain the electron conductivity. However, the high-rate performance is still a serious problem of the LFP cathode even if CNTs are mixed with LFP as the conductive additive.

It is well known that the CH₄ decomposition reaction using the Ni catalyst grows CNTs on the supporting material. In this study, the Ni(0) particle was supported on LFP and was subjected to the CH₄ decomposition to grow the CNTs on the LFP particle. The 2D XAFS imaging measurements have been performed to demonstrate the reduction of the inhomogeneous progress of the charge/discharge reaction for the CNT-decorated LFP cathode.

The Ni particles was supported on LFP by the impregnation method with the Ni loading of 20 wt%. Nickel(II) nitrate was dissolved into deionized water, and LFP was added into the solution. The mixture was dried at 60 °C for 72 h, and the obtained powder was calcined under air at 300 °C for 3 h. To reduce the Ni(II) species, the sample was treated under the 10 vol% H₂ gas flow with the flow rate of 200 cm³/min at 480 °C. Subsequently, the gas was switched to 10 vol% CH₄ to carry out the CH₄ decomposition reaction and kept for 9 h.

The cathode composite was prepared using the CNT-decorated LFP as the active material by mixing polyvinylidene difluoride as the binder, and it was applied on an Al sheet as the current collector. The cathode using original LFP was also prepared as the control using acetylene black (AB) as the alternate of CNT. The pouch cell for *in-situ* XAFS measurement was assembled using a cathode sheet, a Li anode, two porous polypropylene films as the separator, and 1 mol/dm³ LiPF₆ solution dissolved in a mixture of ethylene carbonate and ethyl methyl carbonate. The *in-situ* 2D XAFS imaging measurements were carried out at BL-4 of the SR center [2].

Figure 1 shows the chemical state maps measured for two cathodes with the state of charge (SOC) of 70%. The average oxidation state of Fe was evaluated using the XANES spectra of the cells before charge (SOC 0%, blue pixel) and fully

charged (SOC 100%, red pixel). As shown in Fig. 1(A), several blue spots were observed in the control LFP cathode as in the previous work [1], indicating the inhomogeneous progress of the discharge reaction. On the other hand, such the spots were not observed in the case of the CNT-decorated LFP cathode as shown in Fig. 1(B). The present results clearly demonstrate that the CNT decoration of LFP by means of the CH₄ decomposition using the Ni catalyst diminishes the spatial inhomogeneity of the electrode reaction. The reaction-delay area where the discharge reaction does not precede until SOC 70% are caused by the poor electron conductivity in the cathode plane. The microscopic CNT decoration of LFP improves the electron conductivity. Furthermore, the discharge capacity of the CNT-decorated LFP cathode was found to be *ca.* 80 mA h g⁻¹ at the discharge rate of 20 C, which was drastically improved in comparison to the control cathode with the discharge capacity of less than 1 mA h g⁻¹ at 20 C.

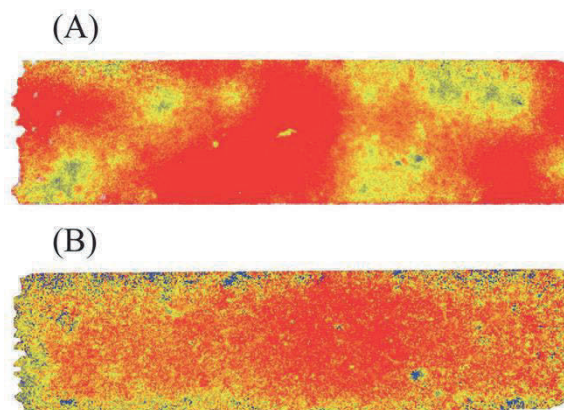


Fig. 1 Chemical state maps of the cathode containing (A) the mixture of LFP and AB and (B) CNT-decorated LFP. The SOC of both cathodes is 70% in discharging process.

Reference

- [1] M. Katayama, K. Sumiwaka, R. Miyahara, H. Yamashige, H. Arai, Y. Uchimoto, T. Ohta, Y. Inada, and Z. Ogumi, *J. Power Sources*, **2014**, 269, 994.
- [2] M. Katayama, K. Sumiwaka, K. Hayashi, K. Ozutsumi, T. Ohta, and Y. Inada, *J. Synchrotron Rad.*, **2012**, 19, 717.