

Structural change of $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ positive electrode material for Li-ion batteries during the first charge-discharge cycle

J. Kikkawa¹, T. Akita¹, M. Tabuchi¹, M. Shikano¹, K. Tatsumi¹, M. Kohyama¹

¹ Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Lithium (Li) ion batteries, essential components of portable electric devices such as laptop computers, attract extensive attention in their application to hybrid cars and electric vehicles. A charge-discharge cycle is performed by reversible extraction/insertion of Li ions in both positive and negative electrode materials, and cyclic oxidation and reduction of transition metal (TM) ions in the positive electrode play essential roles. $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ is an attractive positive electrode material for future electric vehicles since it has high specific capacity ($> 200 \text{ mA h g}^{-1}$) and high voltage ($\sim 3 \text{ V}$) at $60 \text{ }^\circ\text{C}$ [1,2]. Especially, the initial charge capacity reaches about 300 mA h g^{-1} . However, origins of the high initial capacity and large irreversible capacity (100 mA h g^{-1}) at first cycle cannot be explained from the viewpoint of simple redox reaction of TM ions.

Utilizing scanning transmission electron microscopy-electron energy-loss spectroscopy (STEM-EELS) and nano-beam electron diffraction (NBED), we recently found that $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ particle is comprised of Li_2MnO_3 -like (Li_2AO_3 , ($A = \text{Mn}$ and Fe , $\text{Mn} > \text{Fe}$)) with the layered rocksalt structure and α - LiFeO_2 -like nanodomains (α - LiAO_2 , ($A = \text{Fe}$ and Mn , $\text{Fe} > \text{Mn}$)) with the cubic rocksalt structure featured by the cation short-range order [3,4]. The both nanodomains share a common oxygen lattice framework of the cubic close-packed structure [3,4]. As shown in Fig. 1, $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ particles have no grain boundary, differently from a simple polycrystalline composed of Li_2MnO_3 and LiFeO_2 grains with different crystallographic orientations. The chemical nanodomain structure can have profound effects on the high capacity. Much recently, we have found that Li ions in α - LiFeO_2 -like nanodomains are firstly extracted while Li_2MnO_3 -like nanodomains act as structural stabilizers at the first stage of initial charge, which is followed by subsequent Li extraction in the whole region [5]. Nevertheless, detailed mechanisms of Li extraction and insertion in both Li_2MnO_3 -like and α - LiFeO_2 -like nanodomains are still not understood. In this study, we have investigated structural changes of each particle (20–100 nm in size) during the first cycle by NBED utilizing a rather parallel beam of 20–50 nm in diameter.

$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ particles were prepared through coprecipitation, mixed-alkaline hydrothermal and calcination processes at $850 \text{ }^\circ\text{C}$ for 1 min in air [1,2]. First charge/discharge cycle was performed with coin-type cells using a metallic Li negative electrode and a 1 mol solution of LiPF_6 in EC/DEC (1 : 1) as electrolyte in the voltage range of 2.0–4.5 V at the current density of 42.5 mA g^{-1} . The positive electrodes were taken from the cells at the end of charge (4.5 V) and then discharge (2.0 V). The extracted electrodes were rinsed with a small amount of dry solvent (DMC) to remove residual electrolyte and dried to obtain powders for following microanalysis. NBED patterns were collected from each single nanoparticle in a transmission electron microscope (JEM-3000F).

Figure 2 shows NBED patterns from $\text{Li}_{1.2-x}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ before the charge ($x = 0$), after the charge ($x = 0.99$) and after the charge and then discharge (cycle) ($x = 0.26$) with the $[241]_{\text{hex}}$ electron incident direction. Crystal structure is clearly changed after the charge and basically recovered again after the cycle in Fig. 2. We have observed this kind of structural recovery with other crystallographic orientations. The changes in NBED patterns cannot be explained by a simple assumption that Li are extracted from original octahedral sites. NBED patterns after the charge can be attributed to an AB_2O_4 type spinel structure with the space group $Fd\bar{3}m$, where the A and the B cations are located at tetrahedral $8a$ and octahedral $16d$ sites, respectively. It is very likely that some Li or TM ions move from original octahedral sites to

tetrahedral sites during the charge and vice versa during the discharge. We have also found that the AB_2O_4 type spinel structure exists as tiny grains (< 10 nm in size) in each particle. Such tiny AB_2O_4 spinel grains can be annihilated again during the discharge, differently from irreversible formation of bulk spinel $LiMn_2O_4$ in $LiMnO_2$ crystals and thus fatal deterioration in battery performance. We discuss the mechanism of the first charge and discharge process associated with origins of the high capacity and irreversible capacity.

Acknowledgements. This work was financially supported by METI and NEDO, Japan.

References

- [1] M. Tabuchi et al. J. Electrochem. Soc. **154** (2007) A638.
- [2] M. Tabuchi. Et al. J. Power Sources **174** (2007) 554.
- [3] J. Kikkawa et al. Appl. Phys. Lett. **91** (2007) 054103.
- [4] J. Kikkawa et al. submitted, review in process (2008).
- [5] J. Kikkawa et al. submitted, review in process (2008).

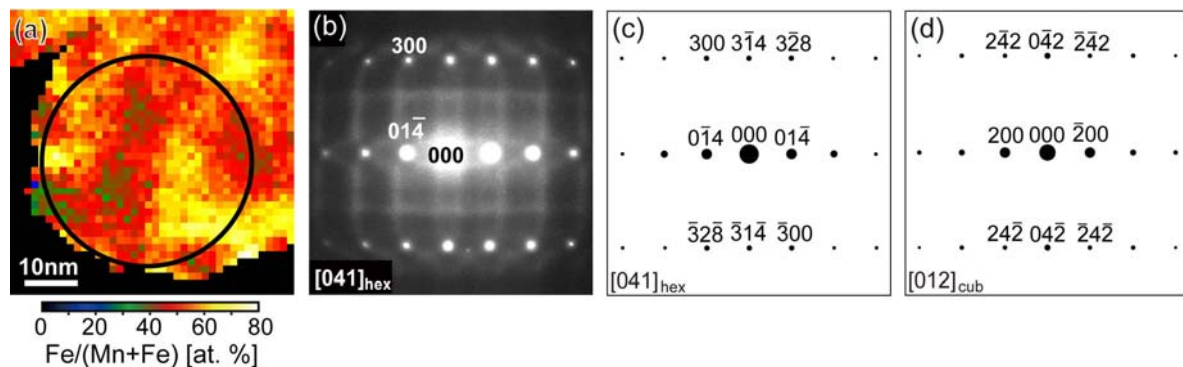


FIG. 1. (Color) (a) Map of iron concentration, Fe/(Mn+Fe). (b) NBED pattern from the circled area in (a), showing the single crystalline feature with diffuse scattering. Simulated ED patterns of (c) the layered rocksalt structure (Li_2MnO_3 -like phase, space group $R\bar{3}m$) and (d) the cubic rocksalt structure (α - $LiFeO_2$ -like phase, space group $Fm\bar{3}m$) with a two phase model [1,2]. Indices are based on the hexagonal cell ($R\bar{3}m$) in (b) and (c) and the cubic cell ($Fm\bar{3}m$) in (d).

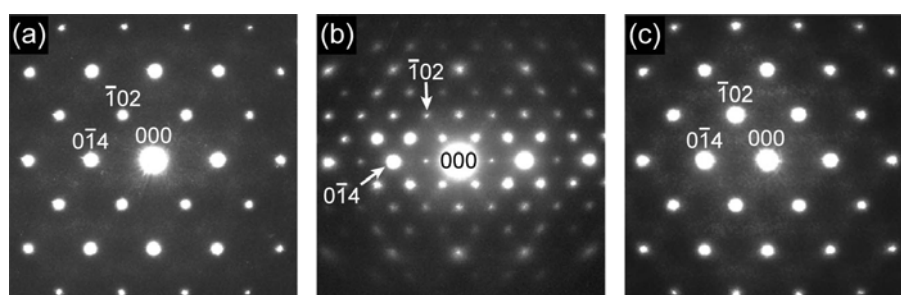


FIG. 2. NBED patterns from $Li_{1.2-x}Mn_{0.4}Fe_{0.4}O_2$ particles (a) before the charge, (b) after the charge and (c) after the cycle along the $[241]_{hex}$ (or $[011]_{cub}$) direction. Indices in (a)–(c) are based on the hexagonal cell (space group $R\bar{3}m$).