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50pm Aberration Corrected *In-situ* Electron Microscopy - How Ion behaves in Lithium Ion Nanowire Battery

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Lithium ion batteries (LIBs) attract much interest, and fundamental understanding of mechanisms enabling longer life for rapid charge-discharge and large capacity in use, particularly, of automobiles. Charge-discharge cycle causes structural phase transition [1] of electrode materials, and rapid cycle results generally in an irreversible cycle. Any irreversible change of the electrode structure can result in capacity fading and/or fracture of the electrode [2]. In order to study dynamical process of charge-discharge cycle, *in-situ* electron microscopy with electrochemical information has been devised to give rich results [3, 4].

An aberration corrected (AbC) electron microscopy (Roo5 microscope) [5] has been applied to solve lithium ion diffusion and phase transition process in LIB, as shown in Fig.1. The electron microscope allowed us to detect the number of lithium ions within each atomic columns of our specimen as demonstrated in Fig.2 [6]. The LIB we developed for *in-situ* study consists of a free standing $LiMn_2O_4$ (LMO) nanowire, ionic liquid electrolyte (ILE) and $Li_4Ti_5O_{12}$ of the negative electrode. The LMO nanowires had lengths of 0.1~0.2mm and diameters of 100nm~200nm. The finest electrode has a single LMO nanowire (Fig.3).

The nanowire-LIB was found to work without capacity fading at high charge/discharge rate (20 minutes for charge of 10nC), and structure of LMO transformed reversibly while the cyclic voltammetry between 3.5 – 5.5 V (Li/Li+), as shown in Fig.4. The nanowire contained three areas having different ion density; lithium-rich, phase boundary (PB), and lithium-poor areas. These areas were moved in a cyclic manner along the nanowire to help the transport of lithium ions (Fig.5). Because of this phase boundary, the nanowire electrode had neither fracture, nor capacity fading. Therefore, the LMO nanowire electrode offers opportunity of long life even at high charge rate.

The electron microscope (Roo5) has achieved a sub-50pm resolution, and has capability of resolving lithium ions which are diffusing within the spinel crystals [7]. Future issue and challenge of *in-situ* AbC microscopy is to image every step of the dynamic procedure of ionic charge and potential transport, which cannot be detectable by other method.

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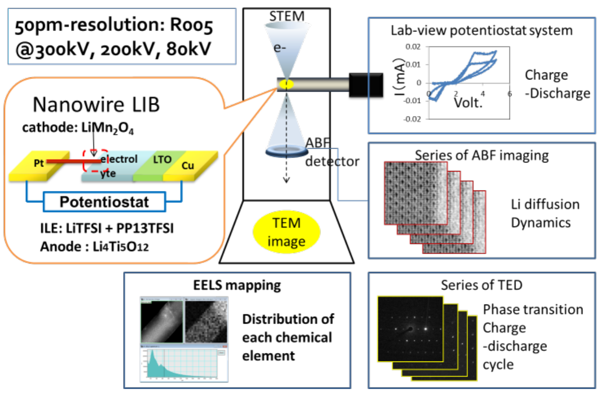

Fig.1 *In-situ* system of nanowire LIB. developed for Roo5 electron microscope

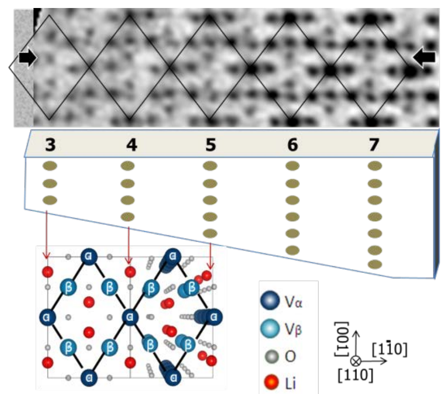

Fig.2 Individual lithium ion imaging by Annular Bright-Field detector

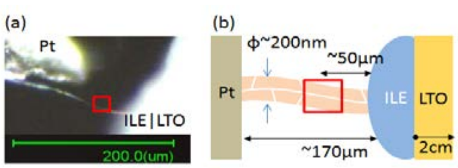

Fig.3 Single nanowire LIB developed for *in-situ* electron microscopy

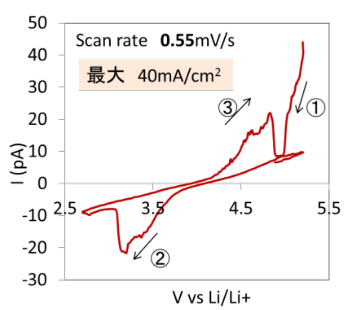

Fig.4 Cyclic voltammograph of a single nanowire LIB in Fig.3

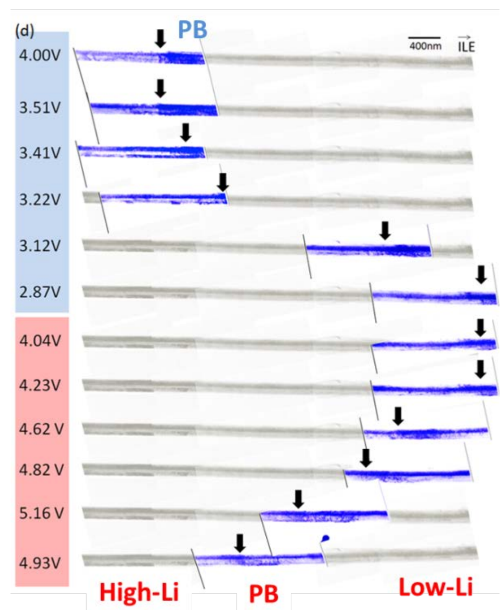

Fig.5 Phase transition of a LMO nanowire during charge-discharge cycle

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