

In-situ STEM Observation of Strain Field Movement in a LiMn_2O_4 Nanowire Battery

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To understand lithium ion transport behavior is an issue for improving the performance of lithium ion batteries. Lithium insertion or extraction reaction in most lithium ion battery (LIB) electrode materials causes lattice parameter change. It leads local strain field change. Thus, measuring strain field during charge-discharge cycles allows us to know how lithium ions move inside a LIB material.

There are several methods to measure local strain field [1-3]. Among them, scanning moiré fringe (SMF) method is reported to use interference between scan raster of scanning transmission electron microscope (STEM) probe and a lattice plane of a crystal [4]. SMF method has some advantages: SMF image can be taken easily by controlling scan raster distance and direction, and strain field movement can be detected by controlling scan speed.

In this study, we have demonstrated in-situ observation of strain field movement inside LiMn_2O_4 cathode during a charge-discharge cycle by using SMF method. The in-situ observation was performed by using our developed nanowire battery which consists of nanowire LiMn_2O_4 cathode, ionic liquid electrolyte and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode [5-6]. The nanowire-battery was loaded in our homemade electrical biasing double-tilt TEM holder. The LiMn_2O_4 nanowire in the nanowire-battery was observed by annular bright field (ABF) imaging [7-8] of STEM using an aberration corrected TEM, R005 at 300 kV. The convergent semi-angle was 30 mrad. The inner-outer semi-angle of ABF detector was 15-30 mrad. Simultaneously electrochemical properties were measured by cyclic voltammetry. The voltage was scanned from 2.20 to 4.50 V vs Li/Li^+ at scan rate of 0.55 mV/s. The measurement was performed by source-measurement unit, Keithley 2635A.

The SMF image was taken by tilting the scan direction slightly from the (111) lattice plane of the LiMn_2O_4 nanowire in order to enhance the sensitivity of the strain field (Fig. 1): the strain change of about 0.1 % was detected. As shown in Fig. 1, the moiré fringe is rotated when the spacing of the lattice fringe is expanded or shrunk.

The moiré fringe was straight without charging or discharging the nanowire battery. However, we found

that the moiré fringe was bent into the shape of mirrored “S” when lithium extraction or insertion reaction occurred. The “S” moiré indicates that the lattice spacing is gradually expanded and shrunk. Such an “S” moiré was observed discretely in the series of STEM images, indicating that the strain field was not caused by the nanowire own structure. Since upper-half and lower-half of “S” moiré was observed in sequentially obtained two STEM images, it indicates that the strain field moved along the nanowire during a charge-discharge cycle. From the series of STEM images, the estimated velocity of the strain field moving was same order with the velocity to lithium movement estimated from simultaneously obtained cyclic voltammetry curve. Therefore, we conclude that the strain field movement corresponded to the movement of lithium ions due to charging or discharging. From the analysis of SMF images, the detail of lithium transport behaviour will be discussed [9].

References:

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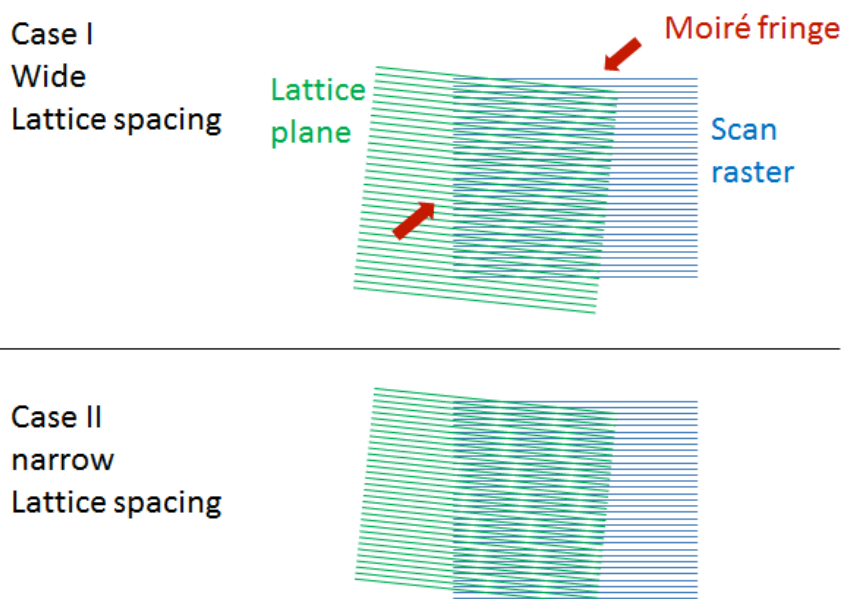


Figure 1. Schematic illustration of scanning moiré fringe method used in this study (rotation moiré). Scan raster (blue) is slightly tilted from lattice plane (green). When lattice spacing is changed (case 1 and case 2), the angle and spacing of moiré fringes (as shown by red arrows) are changed largely.