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Phase Transformations and Structural Changes in the $Li_4Ti_5O_{12}$ Spinel Monitored Using an *in situ* Substrate Curvature System

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A home-built substrate curvature setup was utilized to monitor changes of the volume of $Li_4Ti_5O_{12}$ material, known as “zero strain” anode material [1], during lithiation and delithiation. The measurement data consists of very accurate tracking of mechanical stresses that are due to volume changes caused by the electrochemical reactions. This method is highly suitable for detecting phase transformations as will be shown for the case of $Li_4Ti_5O_{12}$.

In the experiments conventional particle based electrodes consisting of $Li_4Ti_5O_{12}$, carbon black, and PVdF on a Cu current collector are used. The measurements occur in a dedicated test cell where the electrode is mounted on a borosilicate cantilever. The stress of the electrode is calculated using the bending of this cantilever which is monitored by laser deflection (Figure 1).

Stress amplitudes of smaller than 100 kPa are obtained during galvanostatic cycling between 1.45 V and 1.65 V (Figure 2). A linear tensile rise is observed during lithiation, which shows that the particle size reduces as $Li_4Ti_5O_{12}$ is lithiated to $Li_7Ti_5O_{12}$ during the characteristic two phase transition regime on the plateau at 1.56 V. The measurements show a strong stress excursion once the voltage deviates from this plateau. The stress excursions occur during both lithiation and delithiation. The characteristic features of this stress signal will be discussed in terms of diffusion, over- and underlithiation of individual phases and surface effects in the electrode particles.

The stress excursions that occur when this material is lithiated down to 80 mV are about 70 times larger than what is found on 1.56 V plateau. This observation indicates that that the excellent cycleability of $Li_4Ti_5O_{12}$ should be reconsidered for cycles down to low voltages versus lithium [2].

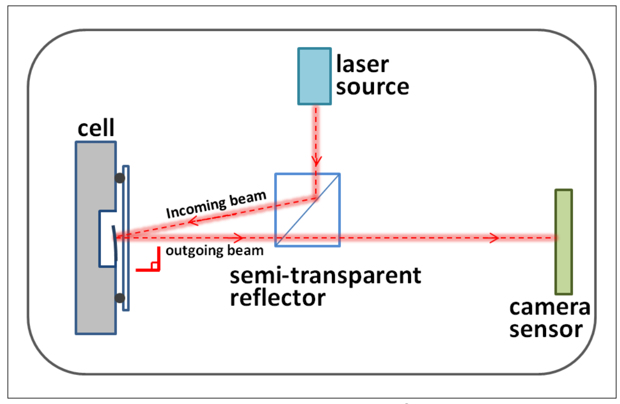

Figure 1: Schematic representation of the experimental setup of the curvature setup showing the optical path and the cell with a cantilever mounted. Note that the curvature of the cantilever and the angle of the incoming beam are exaggerated.

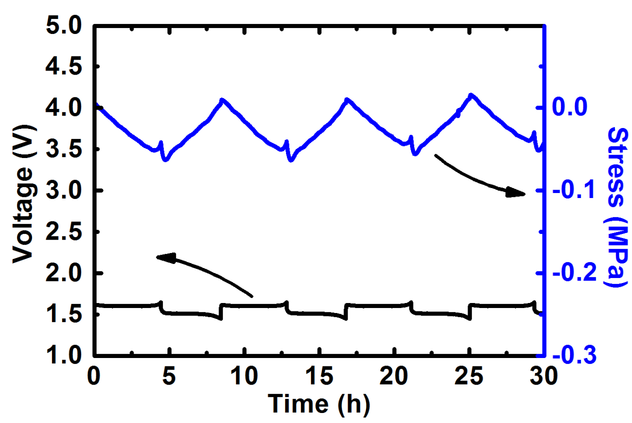

Figure 2: LTO electrode potential and stress variations measured during galvanostatic cycling between 1.45 V and 1.65 V. i.e. within the “zero strain” regime, at a rate of C/5.

[1] T. Ohzuku, A. Ueda, N. Yamamoto, *Zero-Strain Insertion Material of $Li[Li_{1/3}Ti_{5/3}]O_4$ for Rechargeable Lithium Cells*, J. Electrochem. Soc. **142**(5) (1995) 1431
[2] Z. Choi, D. Kramer, R. Mönig, *Correlation of Stress and Structural Evolution in $Li_4Ti_5O_{12}$-Based Electrodes for Lithium Ion Batteries*, J. Power Sources **240**(15) (2013) 245–251