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In situ characterization of charge rate dependent stress and structure changes in V_2O_5 cathode prepared by atomic layer deposition

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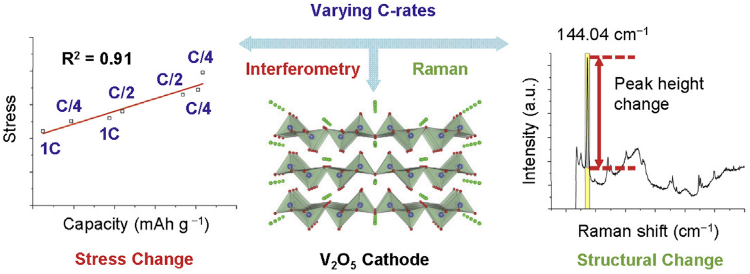
HIGHLIGHTS

- Investigated effects of varying C-rates on stress and structure changes in V_2O_5.
- A linear increase in the stress as a function of x in $Li_xV_2O_5$ is observed.
- C-rate does not directly contribute to larger intercalation stress.
- A rapid increase in disorder within $Li_xV_2O_5$ is correlated with higher C-rate.

GRAPHICAL ABSTRACT



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ABSTRACT

The insertion/extraction of lithium into/from various host materials is the basic process by which lithium-ion batteries reversible store charge. This process is generally accompanied by strain in the host material, inducing stress which can lead to capacity loss. Therefore, understanding of both the structural changes and the associated stress – investigated almost exclusively separate to date – is a critical factor for developing high-performance batteries. Here, we report an *in situ* method, which utilizes Raman spectroscopy in parallel with optical interferometry to study effects of varying charging rates (C-rates) on the structure and stress in a V_2O_5 thin film cathode. Abrupt stress changes at specific crystal phase transitions in the Li–V–O system are observed and the magnitude of the stress changes with the amount of lithium inserted into the electrode are correlated. A linear increase in the stress as a function of x in $Li_xV_2O_5$ is observed, indicating that C-rate does not directly contribute to larger intercalation stress. However, a more rapid increase in disorder within the $Li_xV_2O_5$ layers is correlated with higher C-rate. Ultimately, these experiments demonstrate how the simultaneous stress/Raman *in situ* approach can be utilized as a characterization platform for investigating various critical factors affecting lithium-ion battery performance.

1. Introduction

Lithium-ion batteries (LIBs) provide high energy density while being light-weight and compact, powering a variety of devices such as smartphones, laptops, and desktop computers. New applications

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such as electric and hybrid vehicles demand even higher energy density, longer cycle life, lower cost, and improved safety [1,2]. Therefore, a considerable amount of research has been directed towards developing new electrode materials. A major challenge in these efforts has been characterizing and understanding these materials while batteries are in a state of operation [3].

Different electrode materials react with Li in a various ways, such as intercalation or alloying [1,4,5]. Irrespective of the exact mechanism, stress generation due to lithiation has been demonstrated to produce cracks or fractures in the host material which result in capacity loss and ultimately failure of the battery. In addition to stress, the host material can experience significant structural and chemical changes such as phase transitions [6–8]. Therefore, measurement techniques which acquire stress and structural evolutions in real time could be useful for understanding mechanisms of LIB degradation and advancing battery performance.

Recently, significant progress has been made with *in situ* techniques based on X-ray diffraction (XRD), scanning transmission X-ray microscopy, and transmission electron microscopy (TEM) in structural characterization of LIB electrodes [9–15]. Compared to the aforementioned techniques which reply on complex electrochemical cells and bulky external equipment, Raman spectroscopy is an alternative method for probing structural changes of LIB electrodes with sub-micron spatial resolution in a relatively simple experimental set up readily compatible with liquid electrolytes and without the need for high vacuum. Raman spectroscopy utilizes inelastic scattering of monochromatic photons by the electrode sample, which can acquire information such as crystallinity/disorder, strain, and chemical composition including Li content [7,16]. *In situ* Raman spectroscopy has been widely applied, from graphite and other carbonaceous materials, to transition metal oxides-based compounds, or solid electrolyte interphase formation [7,17]. Additional insights into the battery operation and degradation mechanisms, as well as identifying which phases are present during abrupt changes in stress, can be achieved by combining *in situ* Raman spectroscopy with stress measurement.

In addition to the characterization of structural changes, significant advances have been made in *in situ* mechanical strain/stress characterization of LIB electrodes using a variety of approaches [18–22]. Among these techniques, the multi-beam optical stress sensor (MOSS) has proven to be an effective method for analyzing the stress evolution in LIB thin film electrodes during battery operation. This technique utilizes a silicon substrate coated with a passivation layer, a current collector, and a thin film active battery material of interest. The stress generated in the active material changes the curvature in the wafer which is measured using an array of parallel laser beams. The curvature change is determined by measuring relative changes in the spacing between the reflected beams, and the resulting stress is calculated using the Stoney equation [20]. While this technique is advantageous for mechanical strain/stress characterization, the experimental setup hinders direct access to the electrode which limits its potential integration with other methods that are capable of characterizing structural evolution in the electrode. Additionally, the stress value calculated using this technique is averaged over the entire wafer-scale. Therefore, the MOSS technique gives the best results when it is applied for materials that experience spatially homogeneous strain/stress.

In this work, we investigate the stress and structural changes in an ALD-deposited thin film $Li_xV_2O_5$ electrode over multiple discharge/charge cycles using an *in situ* characterization platform. Despite large theoretical capacity of ~450 mAh/g, $Li_xV_2O_5$ has not been widely adopted in commercial cells in part due to lower voltage *vs.* Li compared to other Li intercalation oxides such as Li_xCoO_2, and in part due to the complexities of the several phase transitions occurring during Li insertion/extraction reactions and how these relate to battery performance. Previously, C-rate variation has been identified as an important factor affecting battery performance [23–25], and the impact of high C-rate on the structure and associated stress in the electrode have been analyzed. The *in situ* platform utilizes a microelectromechanical systems (MEMS) optical sensor integrated with Raman spectroscopy to enable characterization of both the stress and structural changes in the electrode simultaneously. Our results reveal abnormal stress changes when the $Li_xV_2O_5$ electrode experiences α- to ε-phase and ε- to δ-phase transitions. Additionally, these abnormal stress changes have been observed at higher lithium content in $Li_xV_2O_5$ when the electrode is cycled at higher rates, and the magnitude of the stress changes have been correlated with the amount of lithium inserted into the electrode. Moreover, we find signs of a more uniform lithium concentration throughout the electrode with decreasing electrode thickness at the same C-rate. We are also able to analyze Raman peak intensity changes of the translational mode at low frequency (144 cm^{-1}) as a function of x in $Li_xV_2O_5$, showing a faster increase of disorder within the $Li_xV_2O_5$ layers when the electrode is cycled at higher C-rates.

2. Methods and experimental

The MEMS optical sensor (Fig. 1a) used in this work is composed of an array of flexible circular membranes. These membranes divide the sensor into two cavities, referred to as the 'optical' and 'battery' cavities. The optical cavity is formed by anodically bonding glass to a silicon wafer. The battery cavity, which is much deeper, is formed on the other side of the membrane (Si_3N_4, 700 nm) coated with an insulating layer (SiO_2, 250 nm), a current collector (Cr/Au, 15/10 nm), and an active battery material (V_2O_5, 200 nm). The battery cavity simultaneously provides a channel for the liquid electrolyte. The detailed sensor fabrication procedure is described in our previous work [21].

The V_2O_5 thin films are deposited in a BENEQ TFS 500 atomic layer deposition (ALD) reactor by alternating pulses of vanadium triisopropoxide (VTOP) and ozone at 170 °C. The V_2O_5 deposition rate is measured as 0.81 Å/cycle. The V_2O_5 was deposited for 2470 cycles toward a target thickness of 200 nm. The mass of the active material is measured with a high precision microbalance (Mettler Toledo, XS105 dualRange, 1 μg) before and after the deposition.

Packaging for the sensor is achieved using a modified coin cell with an optical window. First, the optical window (5 mm in diameter) is machined into the coin cell cap (LIR2032), and double-sided adhesive aluminum tape (1170 tape, 3M) is placed between the cap and the sensor. A hermetic seal and electron transport are achieved by adhesive aluminum tape. The active material deposited on the sensor and metallic lithium (Sigma Aldrich) pressed against a stainless steel disc serve as the cathode and anode, respectively. A polymer separator (Celgard® 3501) is placed between the two electrodes and soaked with liquid electrolyte (1 M $LiPF_6$ solution in ethyl carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume), Novolyte Technologies). The cell is closed in an argon filled glove box with oxygen concentration of less than 0.1 ppm.

The assembled coin cell is connected to a potentiostat (Compactstat, Ivium Technologies) and placed under a Raman microscope for galvanostatic testing (Fig. 2). This *in situ* experimental setup utilizes a Raman microscope (Yvon Jobin LabRam ARAMIS, Horiba, Ltd.) where the white-light illumination source is replaced with a despeckled 532 nm green laser (CPS532, Thorlab Inc.) for monitoring the membrane deflection using optical interferometry (Fig. 2, interferometric laser). The same microscope is used for monitoring the structure changes of the electrode using a 532 nm