Design of advanced thick anode for Li-ion battery by inserting a graphite/polymer buffer layer: An in-situ mechanical study

Wenduo Zeng [a, b], Junheng Xing [a, b], Jimmy Ching-Ming Chen [a], K.Y.Simon Ng [b], Kenzo Oshihara [c], Mark Ming-Cheng Cheng [a, *]

[a] Department of Electrical and Computer Engineering, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202, United States
[b] Department of Chemical Engineering and Materials Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI 48202, United States
[c] Nissan Technical Center, 39001 Sunrise Dr, Farmington Hills, MI 48331, United States

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ABSTRACT

In this paper, silicon containing thick anode electrodes were investigated to provide a higher energy density and capacity for EV/HEV applications. In our study, a facile technique of adding a mechanical buffer between thick active material and current collector is proposed and tested by an in-situ measurement using white light interferometry. The electrodes with a modified structure deliver a significant improvement to mechanical stability as well as battery performance compared to conventional electrodes with the original structural design. Therefore, the methodology demonstrated here can probably be used to mitigate the deteriorating effect of mechanical failure in silicon-based electrodes, in which volume variation is usually considered as a severe issue, of lithium ion batteries.

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1. Introduction

The reality of exhaust gases of automobiles being accounted for a large portion of air pollution and the gradual depletion of fossil fuel has generated a huge demand for emerging hybrid electric vehicles (HEV) and electric vehicles (EV) [1–5]. However, traditional lithium ion batteries (LIB) have relatively low volumetric and gravimetric energy densities for electrified vehicles. In order to address this issue, many researchers have investigated new materials with higher energy densities, such as silicon, to replace the traditionally used carbon-based electrode materials in anodes. Nevertheless, silicon could not maintain acceptable cyclability and stability due to inevitable mechanical failure during cycles, causing issues such as cracking of materials and delamination of electrodes from current collectors [6,7]. Numerous structures have been proposed to facilitate stress/strain relaxation and transport of lithium ion, including silicon nanotubes, silicon nanowires, micro/nano-porous silicon, and hybrid silicon/carbon nanostructures [8–12]. While these approaches have been shown effective, it is still

challenging for mass production of thick anode electrodes containing silicon, limiting their potential for commercialization. In fact, most studies of nanomaterials use very limited amount of active materials, and it is not clear if they can provide sufficient capacity for EV/HEV in a cell level, especially for long-distance drive.

In conventional LIB, the anodes are typically made of graphite particles mixed with polyvinylidene fluoride (PVDF) binders on the copper current collector. Combination of thick graphite electrode and silicon materials represents an attractive approach for practical EV/HEV applications [13,14]. However, this design still faces poor mechanical stability where the electrode is typically delaminated from the current collector after a long cycle [15]. In order to mitigate this adverse effect, a new design of advanced LIB electrodes is proposed in this paper, in which a "buffer layer" is added between the active material and the current collector. The buffer layer is designed to have an intermediate elastic modulus to limit the large strain (volume expansion) difference between the active material and the current collector. It is expected the characteristic of the interface between the active material and the current collector could be improved, leading to better structural stability. To further validate the improvement of structure deformation for the novel designed battery electrode in a quantitative way, white light

interferometry (i.e. WLI) is utilized to in-situ measure the deformation of electrodes during charging and discharging. In the literature, real-time stress measurements of battery material are typically conducted by multiple beam optic sensors (MOS) [16–21], which required samples to be in a wafer scale and with a thick supporting substrate of lower sensitivity [22,23]. Herein, we demonstrate a new experimental technique using cantilever-shaped microstructures made of conventional electrode materials. Since copper is mechanically elastic and electrochemically inert during cycling, suspended copper cantilevers would be deformed thanks to the volume expansion of active materials during electrochemical reactions [24,25].

The paper presents a comparative study of how the buffer layer between the conventional active material layer and the current collector has an effect on electrode deformation and electrochemical performances. The theoretical capacity is 372 Ah kg^{-1} if made of pure graphite [1]. To increase the capacity, 6% silicon was added. SEM and EDX mapping were conducted to demonstrate the specific layered-structures of the modified and the original samples. Moreover, in-situ deformation of the cantilever electrodes was characterized by WLI to indicate the differences of deformation between electrodes with different layer structures. Also, electrodes with different design were tested in coin cells to show the effect of this structural modification on battery performances.

2. Experiments

2.1. Electrode preparation and cell assembly

The anode (original sample) was made as silicon/graphite composite, of 6% of silicon particles (crystalline, 5−10 μm), 10% of PVDF (Kureha KF1100) and 84% of mesocarbon microbead graphite (MCMB, 15−20 μm) coated onto the current collector layer of a thickness of 20 μm. The layer of active materials was controlled as 40 μm. Also, the sample with a buffer layer uses the same material, with the addition of an insertion of buffer layer (10% of PVDF and 90% of MCMB graphite, thickness of 30 μm) between active material layer and current collector. The cantilevers were machined using high-energy short-pulse laser to remove excess active materials and copper. The as-prepared cantilever was mounted into a home-made cell and the experimental setup is shown in Fig. 1c, where a 3D optical microscopy was used to in-situ characterize the deformation of the cantilever-shaped anodes, and the electrochemical cycles were controlled by a potentiostat (Gamry G300). The composite materials of silicon particle and graphite carbon were used as the working electrode, and the lithium foil was employed as the counter electrode. The smooth copper side of cantilevers was faced up. Liquid electrolyte of 1 M LiPF$_6$ in ethylene carbonate (EC) and diethylene carbonate (DEC) with 1:1 ratio was used to fill up the cell chamber. The effective areal capacities were calculated as 3.39 mAh cm^{-2} and 1.35 mAh cm^{-2} for original and modified sample based on their chemical composition and effective area, respectively [1,12]. Since the cantilever electrode was immersed into the electrolyte and covered with a quartz in the cell. The optical length has

been changed. A calibration procedure was performed to compensate the difference in optical lengths between the reflected and reference lights [26]. A liquid lens was added in the path of reference light, which has two quartz windows with total thickness the same of the quartz window in the cell and filled with electrolyte with the same distance between the cantilever and quartz window in the cell.

2.2. Real-time and in-situ strain measurements

WLI was used to measure in-situ 3D profiles. The curvature and deflection were monitored with 3D optical microscope (Bruker Contour GT In-Motion) accompanied with a through transmissive media (TTM). The difference of optical path between height change of the sample surfaces and reflection from a reference mirror can be detected by an imaging sensor. The pattern of interference would be transformed as varying image signal, demonstrating the deformation of tested sample [27,28]. Corresponding deformation and stress evolution in anodes during electrochemical cycles were measured by detecting the curvature and deflection variation of the cantilever-shaped electrodes.

During lithiation and delithiation in electrochemical cycles, the insertion and extraction of lithium ions into and out of active materials layer would cause corresponding expansion and shrink. By fabricating the working electrode into the shape of cantilever, the stress caused by expansion and shrink in active material layer would induce the whole bilayer or triple-layer cantilever to deform and introduce the mechanical behavior of curling up or down of the cantilever structure. The corresponding change of cantilever curvature could be monitored using WLI. This procedure could be analogous to the case of thermal expansion of a multi-layer cantilever, in which different layers possess varying thermal expansion coefficient (α_1, α_2). The curvature could be correlative to the thermal strain, ($\alpha_1 - \alpha_2$) $\triangle T$, with the relationship as:

$$\kappa = \frac{6(1 + m)^2 (\alpha_1 - \alpha_2) \Delta T}{3(1 + m)^2 + (1 + mn)(m^2 + \frac{1}{mn})} \frac{1}{h_t} \tag{1}$$

where h_t means the total thickness of bilayer cantilever, $n = E_1/E_2$ and $m = h_1/h_2$. E_1, E_2 and h_1, h_2 mean Young's modulus and thickness of the coated thin film and the substrate, respectively [29].

In our current study, the mechanical stress is induced by the volume changes during electrochemical cycling instead of thermal expansion, therefore the thermal strain term in Eq. (1) is replaced by a free actuation strain of the Si/MCMB during lithiation and delithiation when it is not attached to the copper. When an additional buffer layer is added, the cantilever beam turns out a trilayer structure, and the bilayer Timoshenko equation needs to be modified as [30]:

$$\kappa = \frac{6m_a n_a \left(1 + m_a + m_b^2 n_b + m_b (2 + m_a n_b)\right) \alpha}{\left(1 + m_b^4 n_b^2 + 4m_a n_a + 6m_a^2 n_a + 4m_a^3 n_a + m_a^4 n_a^2 + 4m_b^3 (n_b + m_a n_a n_b) + 6m_b^2 (n_b + 2m_a n_a + m_a^2 n_b n_a) + 4m_b (n_b + 3m_a (1 + m_a) n_a + m_a^3 n_a n_b)\right) h_{Cu}} \tag{2}$$

Where α is the free actuation train of the Si/MCMB layer, h_{Cu} means the thickness of copper substrate, m_a and m_b mean the ratio of thickness of silicon/graphite layer and buffer layer to copper substrate, n_a and n_b mean the ratio of elastic modulus of silicon/