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Modeling the delamination of amorphous-silicon thin film anode for lithium-ion battery

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HIGHLIGHTS

- Computational study of electrochemical cycling induced film delamination has been undertaken.
- Current collector mechanical properties significantly influence cycling response.
- Elasto-plastic current collectors show partial delamination of the thin film.
- Absence of interfacial delamination in thin Si film on low modulus elastic substrate.

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ABSTRACT

Sputter-deposited amorphous silicon thin films on metallic copper current collectors are widely studied as lithium-ion anode systems. Electrochemical results indicate these electrodes exhibit near theoretical capacity for first few cycles; however delamination at the thin film–current collector interface causes rapid capacity fade leading to poor cycling performance. Primary reason for this interfacial delamination is the mechanical stress generated due to colossal volume expansion of silicon during lithiation. The focus of the current study is to present a mechanistic understanding of the role of mechanical properties of the current collector on this characteristic delamination behavior during electrochemical cycling. Toward this end, we have developed a computational framework that accounts for the coupled diffusion induced large deformation in silicon, elasto-plastic deformation of the current collector, as well as the nucleation and propagation of interfacial delamination. We have also performed a detailed parametric study to investigate the effect of mechanical properties of the current collector on the delamination of the thin film–current collector interface. We have accordingly determined that current collectors with low elastic modulus such as graphite can completely suppress interfacial delamination. Our analysis thus provides a sound mechanistic approach for designing next generation Si thin film anodes with improved capacity retention.

1. Introduction

Lithium-ion batteries (LIBs) at present are widely considered as the flagship energy storage system for a variety of portable consumer electronic devices and transportation systems. Sony introduced first commercial LIB based on $LiCoO_2$ and carbon anode in 1991 to be used primarily in portable consumer electronic devices. Since then, the LIB system and the area in general, has witnessed tremendous research activity focused at primarily improving the capacity and cycling performance to support the increasing energy storage demands of new and emerging portable and consumer electronic devices, while extending its application to transportation systems. Accordingly, the application of LIBs today extends exclusively not only to laptops, camcorders and cameras but also to smart cellular phones, hybrid and plug-in electric vehicles (HEV's, PHEVs), all electric vehicles (EVs), as well as several advanced aerospace applications. The current universally accepted energy

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storage system status shared by LIBs is a consequence of intense research directed particularly in the cathode area, although over the last few years since the mid 2000 there has been a conscious effort directed at developing new anodes and improved electrolytes. Despite this, graphite is still the preferred and commercially used anode material in LIBs to date exhibiting a theoretical capacity of 372 mAh g^{-1}.

With the growing energy storage demands and continued miniaturization of advanced portable and consumer systems, there is a stringent need for longer lasting portable energy storage systems with high energy and power densities. Thus with identification and improvements in the cathode area, there is a need for the development of new anodes. In this respect, silicon based anodes have emerged as the front runner due to its very high specific capacity (3580 mAh g^{-1}). However, silicon undergoes colossal volume expansion during lithiation ($\sim$300%), and the diffusion-induced stresses result in the formation of cracks with deleterious effects on the battery performance. Furthermore, as is known, the volumetric expansion related stresses result in delamination of silicon from the current collectors leading to loss of electrical contact causing poor cycling performance of this particular configuration [1]. To improve the mechanical integrity during electrochemical cycling and thus help retain the capacity, various silicon based anode configurations in the form of nanotubes, nanowires, core shell structures, single/multi layer thin films, patterned nanostructures, etc. have been synthesized and tested for their electrochemical performance in LIB [2–4]. Amorphous silicon based thin film anodes in particular have shown potential to be the next-generation anodes due to their near-theoretical performance of 3580 mAh g^{-1} and reduced influence of volumetric stress related catastrophic failure due to the available free volume for accommodation of the stresses [5].

1.1. Mechanical properties of the interface: a vital parameter

Mechanical integrity of the thin film–current collector interface and hence the performance of *a*-Si thin film anode depends on the mechanical properties of the interface and the current collector, as well as the geometric factors such as thin film dimensions. Modification of the substrate surface morphology to increase the adhesion of *a*-Si thin film with the substrate has shown to improve the cycling performance [6]. Annealing the *a*-Si thin film deposited on Cu substrate at high temperature is also known to improve the adhesion between the two surfaces by interdiffusion of Si and Cu [7]. Thus, it has been reported that better attachment of thin film with the substrate delays the interfacial crack propagation resulting in lower capacity fade. Recently, patterning of the thin film has garnered attention as a possible avenue to mitigate delamination at the interface [8–10]. In a series of papers, Gao and coworkers have theoretically studied the effect of size of thin film islands on interfacial delamination [11–14]. They have determined the existence of a critical size of the islands, below which delamination will not occur and further propagate. Another strategy to suppress delamination that has not garnered much attention yet is the proper choice of current collector and its mechanical properties to safely accommodate the stresses generated during electrochemical cycling of the anode. Recent experiments show that the presence of an interfacial layer of amorphous carbon between *a*-Si thin film and substrate results in excellent capacity retention of the thin film anode [15]. Motivated by this observation, we present for the first time a systematic study of the effect of mechanical behavior of the current collector on the onset and propagation of the interfacial delamination of the thin film anode. We selected elastic modulus and yield strength as the two essential mechanical properties to effectively categorize the performance of the candidate current collector materials. In doing so, the goal is to provide and identify candidate current collector systems that will be conducive for effectively mitigating the deleterious effects of the catastrophic failure in Si.

We accordingly present herein a thermodynamically consistent theoretical framework that considers the large deformation as well as failure response of the anode materials system coupled with the necessary voltage performance of the electrode. We demonstrate predictive capability of the presented model through the simulation of voltage–capacity curves for a thin film configuration subjected to different charge rates. Also, our model can simulate the interfacial crack propagation leading to capacity fade and ultimate failure of the anode. We postulate that a process zone precedes the actual nucleation of a crack, and thus can be modeled using the cohesive zone technique. The presented model includes elastic as well as elasto-plastic behavior of the underlying current collector, and thus can examine the interaction of its passive mechanical response with the active response of *a*-Si. Utilizing this model, we demonstrate the effect of substrate mechanical properties on the delamination of the thin film from the current collector.

The paper is organized into various sections: In Section 2, we detail our modeling framework with an emphasis on initiation and propagation of interfacial delamination. Experimental methods to determine open circuit voltage to be used in our simulation are presented in Section 3 along with the details of the numerical model. The model is validated in Section 4 against experimental voltage–capacity response of a representative thin film anode based half cell. We further demonstrate the predictive capability of our model by simulating the same response for different charge rates, and contrast our findings with experimental ones. We also present a detailed parametric study of interfacial delamination by systematically varying mechanical properties of the current collector. We discuss the simulation results and their implications on the design of thin film anode in Section 5. We compare our findings with experimental results wherever possible. We finally conclude the article by summarizing the merits of the different current collector materials with potential suggestions for future improvements.

2. Model description

Recently a few models have appeared in the literature [16–20] that have focused on coupled diffusion and stress generation in the large deformation regime. Crack propagation in a cylindrical graphite particle [21] as well as in a silicon nanowire due to diffusion induced stress has also been studied [22]. However, the present modeling framework focuses particularly on interfacial delamination of thin film anode from the current collector rather than its bulk disintegration, which is a critical factor affecting the thin film Si anode failure. Importance of this mode of failure on the cyclic performance of thin film based anodes has been studied experimentally by our group a few years ago in the work reported by Maranchi et al. [1]. Possible mechanisms for such failures have also been discussed recently through theoretical considerations [8,11–14]. We complement these research efforts by presenting an experimentally validated comprehensive computational framework that will enable us to investigate the interplay between various electrochemical and mechanical phenomena responsible for delamination of the thin film–current collector interface. The present model hence seamlessly integrates electrochemical charge/discharge cycling with stress-assisted delamination of silicon thin film anode from current collector (see Fig. 1(a)). The Faradaic reaction at the anode/electrolyte interface is modeled using the classical Butler–Volmer approach. Lithium atom (reduced state) further diffuses into the bulk of the anode that undergoes large volume expansion, in turn generating large stresses. A detailed thermodynamically consistent framework