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The mechanics of large-volume-change transformations in high-capacity battery materials

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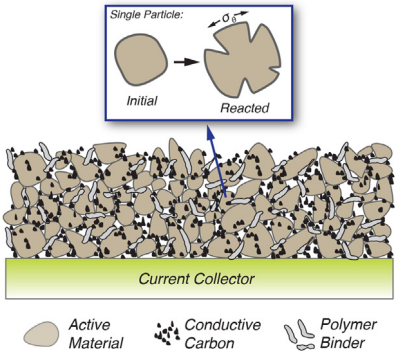
GRAPHICAL ABSTRACT



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ABSTRACT

High-capacity next-generation materials for Li-ion and Na-ion batteries often undergo significant volume changes (up to ~300%) during reaction with Li or Na. These large-volume-change transformations cause mechanical fracture and pulverization of active battery materials, which can have detrimental effects on battery cycle life. Recent years have seen significant efforts dedicated to understanding the mechanics of such large-volume-change transformations in alloying anode materials. This review paper introduces recent work focused on various aspects of the mechanics of alloying anode materials, including *in situ* characterization of real-time reaction mechanisms and mechanical degradation processes, measurements of mechanical properties, measurements and simulations of spatiotemporal stress generation and evolution in active battery materials and structures, and studies on the interplay between chemistry and mechanics during reaction. In addition, mechanical effects across length scales within battery electrode structures are discussed. As demonstrated herein, the improved understanding of the

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mechanics of large-volume-change transformations has been essential for the rational design of durable high-capacity electrodes for Li-ion and Na-ion batteries.

Contents

1. Introduction

Li-ion batteries are established as the most important energy storage technology for portable electronics and electric vehicles [1,2]. Despite the success of Li-ion batteries, emerging applications such as low-cost electrified transportation and grid energy storage require batteries with improved performance characteristics and lower cost [1]. This necessitates the development of new high-capacity, low-cost electrode materials for Li-ion batteries [3–9], and/or the engineering of entirely new battery systems, such as lithium–sulfur, Na-ion, or flow batteries [10–13]. Fundamental scientific and engineering challenges must be overcome in all these cases.

Conventional Li-ion batteries contain electrode materials that react with Li^+ ions via intercalation reactions. This reaction mechanism involves the insertion and removal of Li^+ ions as "guests" within the relatively invariant crystal structure of a host material, with only minor volumetric changes of the host (∼5%–10%) [14]. The small volume changes allow for reversibility over hundreds of cycles, and thus long cycle life. However, these materials have limited lithium storage capacity since the extra atoms within the host structure take up space within the electrode and contribute mass to the battery. A variety of materials are known that have much larger lithium storage capacities because they react via different reaction mechanisms, such as alloying and conversion reactions [15–17]. These reaction mechanisms are characterized by the formation of entirely new phases during reaction with Li^+, and there is often significant (100%–300%) volume expansion/contraction during cycling (Fig. 1 inset). Such extreme volume changes in active material particles have traditionally led to poor cycle life for a number of reasons, including mechanical degradation/fracture of particles and side reactions accelerated by the continually changing surface area. Overcoming these issues would allow for the engineering of Li-ion batteries with higher energy density, and such progress would also enable new materials for Na-ion batteries.

In recent years, it has become evident that the solid mechanics of alloying and conversion materials plays a major role in these extreme-volume-change transformations [5,18]. Transformation strains in individual active particles cause large stresses to exist within these materials due to ion concentration gradients or external/interfacial constraints. These stresses can cause fracture or void growth, and they lead to changes of morphology during cycling. Reaction-induced plasticity and flow are also important aspects of transformations in certain materials that influence the magnitude and spatial distribution of stresses within active material structures. Furthermore, evolved stresses are intrinsically linked to the thermodynamics and kinetics of the electrochemical reaction process via chemomechanical effects; this can have important ramifications for the energy efficiency during charge/discharge of a battery. Finally, large-volume-change materials also exhibit complex mesoscale interactions within battery electrodes: mechanical interactions between particles, as well as interfacial adhesion characteristics, play more important roles than in traditional materials.

Much recent groundbreaking work has been dedicated to fully understanding the mechanical aspects of electrochemical transformations in various alloying and conversion materials. This review paper is meant to provide an overview of recent experimental and modeling efforts in this area, with a focus on alloying reactions of anode materials. The review is organized in the following manner. First, experimental observations of volume changes and fracture processes in various materials will be detailed. Then, studies on the mechanical properties and dynamic stress evolution within active material structures will be presented, along with the current understanding of the influence of stress on the thermodynamics and kinetics of reaction processes. Finally, recent work on the mesoscale and interfacial mechanics of electrode architectures (as schematically shown in Fig. 1) will be discussed. Together, this body of work has provided much new knowledge regarding these unique transformations, and in many cases, fundamental mechanics insights have guided the develop-