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Time-dependent deformation behavior of polyvinylidene fluoride binder: Implications on the mechanics of composite electrodes



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HIGHLIGHTS

- Time-dependent mechanical behavior of PVdF was thoroughly characterized.
- PVdF behaves more like an elastic-viscoplastic material for time-scales of interest.
- Lithiation/delithiation of Si-PVdF composite was simulated with Abaqus FE package.
- Linear elastic assumption of binder leads to inaccurate results.
- Elastic-viscoplastic model predicts mechanics of composite electrode accurately.

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ABSTRACT

The majority of existing battery models that simulate composite electrode behavior assume the binder as a linear elastic material due to lack of a thorough understanding of time-dependent mechanical behavior of binders. Here, thin films of polyvinylidene fluoride binder, prepared according to commercial battery manufacturing method, are subjected to standard monotonic, load-unload, and relaxation tests to characterize the time-dependent mechanical behavior. The strain in the binder samples is measured with the digital image correlation technique to eliminate experimental errors. The experimental data showed that for (charging/discharging) time scales of practical importance, polyvinylidene fluoride behaves more like an elastic-viscoplastic material as opposed to a visco-elastic material; based on this observation, a simple elastic-viscoplastic model, calibrated against the data is adopted to represent the deformation behavior of binder in a Si-based composite electrode; the lithiation/delithiation process of this composite was simulated at different C rates and the stress/strain behavior was monitored. It is observed that the linear elastic assumption of the binder leads to inaccurate results and the time-dependent constitutive behavior of the binder not only leads to accurate prediction of the mechanics but is an essential step towards developing advanced multi-physics models for simulating the degradation behavior of batteries.

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1. Introduction

In a composite battery electrode the polymer binder plays a critical role of providing the electrical network, i.e., electrical pathway, between the active material particles and the current collector, which is necessary for battery operation [1]. The binder adheres the conductive additives and active particles together to provide this electrical network. The loss of electrical connectivity

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due to mechanical failure of the binder is one of the primary degradation (or capacity fade) mechanisms of lithium-ion battery electrodes. For example, the volume changes of active particles during insertion and extraction of lithium (i.e., charge/discharge process) induces a significant amount of stress/strain in the binder and at the binder/current collector interfaces. When these stress/strain levels reach a critical value, the binder will undergo inelastic (permanent) deformation followed by fracture failure; this leads to electrical isolation of some active particles, which prevents them from actively participating in the chemical reactions causing an irreversible loss of battery capacity.

Significant research efforts are underway to design high capacity and durable electrodes that can sustain thousands of cycles

with minimum capacity loss for future energy storage applications, e.g., electric cars. Conventional graphite-based electrodes provide a specific capacity of 372 mA h/g which is inadequate to meet the projected future energy storage demands [2]. Si is a promising anode material as it can provide an order of magnitude higher theoretical capacity (3579 mA h/g) compared to that of conventional graphite-based anodes [3,4]. However, Si electrodes show poor cyclic performance due to large volume changes and the associated stresses. Specifically, Si undergoes approximately ~270% volume change upon reacting with lithium [5] compared to only 10% volume expansion of graphite [6,7]. This level of volume expansion of high energy density electrode materials, such as Si, imposes a deformation on the binder to a greater extent than the traditional graphite-based electrode. Hence, understanding the mechanical behavior, i.e., mechanical strength and deformation characteristics, of polymer binders becomes essential for improving the long-term cyclic behavior of next generation battery electrodes.

Polyvinylidene fluoride (PVdF) is the most commonly used polymer as a binder material in majority of Li-ion batteries [8,9], and it continues to be the primary choice for emerging batteries such as Na-ion [10] due to its superior chemical and electrochemical stability. Several studies [8,11,12] showed that the binder properties can significantly affect the cyclic performance of battery electrodes. Consequently, numerous studies focused on developing new and improved binder materials: nature inspired [13], aqueous solvent-based [14], sidechain-based [15], and others [16,17], but, none of the aforementioned studies investigated the fundamental mechanical behavior of binders. A recent study on the mechanical stress measurements on composite electrode by Sethuraman et al. [18] demonstrated that mechanical behavior of the binder influenced the degradation of electrodes, showing the relative importance of the binder.

The need to understand degradation in batteries has motivated several experimental and theoretical studies of stress evolution, diffusion, and fracture in battery materials; Verbrugge and Cheng [19], Christensen and Newman [20], and Bhandakkar and Gao [21] are some examples of models at a single particle or thin film level. Bower et al. [22] and later Anand et al. [23,24], Zhao et al. [25], Bucci et al. [26] have proposed more comprehensive models which include large deformation kinematics that can simulate the mechanical and electrochemical processes of advanced electrodes such as Si. Some of the recent experimental studies on the advanced electrode materials include Nadimpalli et al. [27,28], Al-Obeidi et al. [29] and Wang et al. [30]. However, major focus so far has been on the mechanics of active materials and not on composite electrodes. Although the models proposed by Christensen [31], Garica et al. [32], Wang et al. [33], Higa and Srinivasan [34], and Xu and Zhao [35] can capture the mechanics and electrochemistry of composite battery electrodes, most of them treat the binder as a simple linear elastic material which is inadequate and does not represent the actual mechanical behavior of polymer binders. One of the reasons for this treatment is the lack of thorough mechanical characterization of the binders.

In general, materials used in batteries such as ceramics (i.e., LiCoO₂ and other transition metal oxides), metals (e.g., Cu, Sn and Al) and other materials such as graphite, Si, and Ge, exhibit a linear elastic response under a moderate amount of stress and either plastic deformation (in case of metals) or failure (in case of ceramics) beyond the elastic limit. This is largely time-independent and the stresses in the material do not depend on the rate at which the strain is applied. However, polymers, such as PVdF, exhibit time-dependent mechanical deformation behavior. This behavior is called visco-elastic if the polymer recovers the deformation when the load is removed and a sufficient amount of time is provided, and is called elastic-viscoplastic if the recovery is not

complete even after a long time (of practical interest). Once the experimental data is available, one can choose the most appropriate constitutive behavior to model the polymer depending on the characteristic time frame of interest and the deformation levels. Although Chen et al. [36] previously studied the linear visco-elastic behavior of PVdF, it was mainly a qualitative study and the focus was not on producing data that is sufficient to develop a constitutive model for binder; moreover, these tests were conducted at a single strain-rate and no explanation was provided why a visco-elastic model was appropriate for PVdF.

The objective of this paper is to characterize the time-dependent mechanical behavior of the polymer binder, specifically PVdF due to its extensive industrial use. Toward that objective, standard uniaxial load-unload tests, uniaxial tests at different strain-rates, and relaxation tests were performed on thin PVdF films. Based on the experimental observations, a simple viscoplastic model has been chosen to represent the PVdF constitutive behavior. The model was calibrated against the experimental data. It should be noted that the experimental data provided here can be used to develop a more elaborate constitutive model depending on the objective and strain levels involved in a particular problem of interest. A user subroutine UMAT was developed based on this simple model and implemented in the commercial finite element package Abaqus. The overall mechanical response of a Si-PVdF composite electrode during the lithiation/delithiation process was simulated using finite element simulations at different C-rates with PVdF modeled as 1) an elastic-viscoplastic material and 2) a linear elastic material. It will be shown that the linear elastic assumption of polymer binder is inadequate, and the elastic-viscoplastic constitutive model for the PVdF binder not only predicts the mechanics of the electrode accurately but also improves the accuracy of battery degradation model predictions.

2. Experimental procedures

2.1. Sample preparation

A uniform PVdF-binder solution was prepared by dissolving 20 wt% PVdF powder (Sigma Aldrich) in *N*-Methyl-2-pyrrolidone (NMP, Sigma Aldrich) and mixing it thoroughly with a magnetic stirrer for 24 h. The ratio of binder to NMP solvent was optimized to yield a desirable viscosity for spin coating process. The PVdF-NMP solution was spin coated on a glass slide at 600 rpm for 60 s using a portable spin coater (VTC-100A, MTI Crop.). The glass slides were cleaned with acetone and isopropanol before spin coating to prevent contamination of samples. The films were cured in a convective oven at 90 °C for 10 h. This process produced films with thickness of approximately 25 μm with a uniformity of ±1 μm within the film. These films were then cut to dimensions as shown in Fig. 1a.

2.2. Mechanical characterization

An experimental setup, shown in Fig. 1b, c, was designed and built to perform the mechanical characterization of PVdF films. This setup is capable of measuring loads and displacements with a resolution of 50 mN and 29 nm, respectively. The samples prepared by the above method, shown in Fig. 1a, were clamped with grips designed to prevent any sliding. A LabVIEW program was used to control the actuators so that the samples can be stretched at a desired speed monotonically as well as cyclically. In addition to recording the load and displacement data, images of the sample during deformation were captured using a 5 mega pixel monochromatic CCD camera (Point grey Inc.) and lens (Fujifilm Inc.) system. A random speckle pattern of black spots were deposited, as

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