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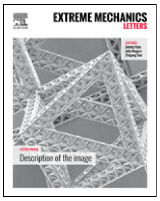

Grid indentation analysis of mechanical properties of composite electrodes in Li-ion batteries

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ABSTRACT

Electrodes in commercial rechargeable batteries are microscopically heterogeneous materials. The constituent components, including active materials, polymeric binders, and porous conductive matrix, often have large variation in their mechanical properties, making the mechanical characterization of composite electrodes a challenging task. In a model system of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ cathode, we employ the instrumented grid indentation to determine the elastic modulus and hardness of the constituent phases. The approach relies on a large array of nanoindentation experiments and statistical analysis of the resulting data provided that the maximum indentation depth is carefully chosen. The statistically extracted properties of the active particles and the surrounding medium are in good agreement with the tests of targeted indentation at selected sites. The combinatory technique of grid indentation and statistical deconvolution represents a fast and reliable route to quantify the mechanical properties of composite electrodes that feed the parametric input for the mechanics models.

1. Introduction

Li-ion batteries play a central role in portable electronics and electric vehicles [1,2]. Technological improvements in rechargeable batteries are being driven by the ever-increasing demand on materials of long lifespan, high energy density, fast charging and power output, low cost, and safe operation [3]. Mechanical stability is an important measure of high-performance batteries. For instance, the drastic change in volume is an intrinsic drawback of high-capacity electrodes [4]. The volumetric strain is linearly proportional to the number of absorbed Li in alloying-type anodes and it reaches over 300% in Si which has the highest theoretical specific capacity [5]. As such, mechanical degradation places a roadblock in the implementation of high-capacity electrodes in commercial batteries. In high-power-output batteries of high current and deep discharge, structural disintegration impedes electron conduction and increases the ohmic and thermal resistance which can result in catastrophic failure of batteries [6]. More recently, mechanical stability becomes a major criterion in the selection of solid electrolyte for solid-state batteries. In addition to possessing appropriate electrochemical properties, polymer electrolyte must exhibit high mechanical strength in order to suppress the dendrite growth of Li metals and to enable large-scale manufacturing of the devices [7,8].

The mechanics perspectives provide important insight in the optimum design of batteries. Numerous theoretical modeling and experiments have been conducted to characterize the large deformation, stress generation, and fracture in electrodes modulated by the electrochemical processes of lithiation and delithiation [9–27]. The mechanical properties of electrodes are prerequisite parameters for the mechanics models. Nevertheless, elastic modulus,

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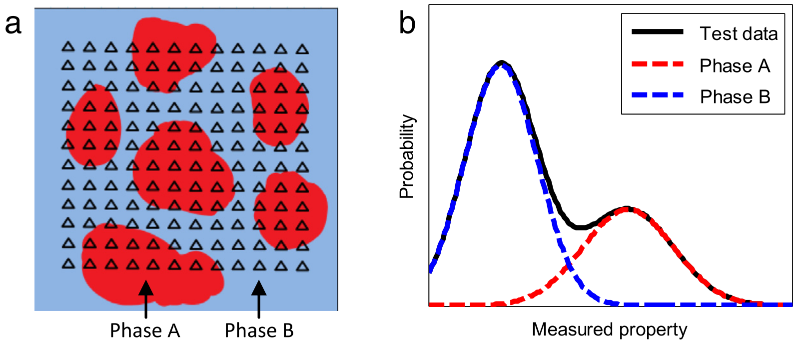

Fig. 1. (a) Schematic of grid indentation on a heterogeneous material. The red and blue colors represent different phases, and the triangles represent individual indentation sites. The indentation size is much smaller than the characteristic size of the phases and the grid spacing is larger than the size of indentation impression. (b) Grid indentation yields a multimodal probability function that allows determination of mechanical properties of the constituent phases. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hardness, and fracture strength of most emerging electrode materials are unknown *a priori* that makes theoretical predictions questionable. The difficulties underlying the experimental characterization on the mechanical properties of battery materials are twofold. First, electrodes in commercial batteries are heterogeneous materials consisting of metal- or ceramic-like active materials, polymeric binders, and porous carbon black (CB) conductive matrix [28]. The constituent components have large difference in their mechanical properties—the elastic modulus changes by 2–3 orders of magnitude for instance. In addition, the mechanical properties of composite electrodes are highly dependent on the packing density of the active material from the elementary powders and tortuosity of the surrounding medium [29]. Determining the mechanical properties of individual phases in the microscopically heterogeneous structures is a challenge. Second, the mechanical properties of active materials may vary significantly with the state of charge, for example, elastic modulus of graphite increases by three fold upon lithiation [30], and Si experiences a transition of brittle behavior in its pure form to a ductile material in the lithiated state [31–33]. Few data are available so far that compile the dependence of mechanical properties of electrodes on the state of charge.

We employ the technique of grid indentation that is suited to measure the mechanical properties of composite electrodes of high heterogeneity at the nano- to microscale [34,35]. Grid indentation relies on a massive array of nanoindentation and statistical deconvolution of experimental data to extract the mechanical properties of individual components. Fig. 1(a) sketches a material composed of two phases of distinct properties. Provided that the indentation depth is much smaller than the characteristic size of the two phases and the grid spacing is larger than the size of the indentation impression, a large number of indentations on the sample surface probe the mechanical properties of either phase with the probability that equals the surface fraction. Assuming that the distribution of the mechanical property of each phase can be described by the Gaussian distribution, grid indentation yields a multimodal probability function that allows determination of properties of each phase, Fig. 1(b). We apply grid indentation to a model system of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) cathode for commercial batteries. $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) is a class of cathode material attractive for the electric vehicle applications [36–39]. NMC is generally comprised of alternating Li and transition-metal layers where the composition of Ni, Mn, and Co can be tuned to optimize the performance in capacity, cyclic rate, electrochemical stability, and lifetime. The mechanical properties of the NMC electrodes have been widely unknown.

We validate grid indentation of the NMC532 electrode by comparing with the results of targeted indentation at selected sites. The maximum indentation depth is carefully chosen to avoid the effect of particle morphology at shallow indentation and the effect of surrounding medium at deep indentation. Grid indentation provides a fast and reliable route to characterize the mechanical properties of heterogeneous composite electrodes and will become a valuable tool in the design of resilient commercial batteries.

2. Experimental procedure and statistical analysis

2.1. Sample preparation

As-received $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532, Toda America) powders, polyvinylidene fluoride, (PVDF, Solvay, 5130), carbon black (CB, Denka, powder grade), and N-methylpyrrolidone (NMP, Sigma Aldrich) were used to prepare NMC cathodes by slot-die coating, which consist of 90 wt% NMC532, 5 wt% PVDF, and 5 wt% carbon black. Detailed fabrication method can be found in Ref. [40]. The areal loading of the NMC cathode was 12.5 mg/cm^2. Samples composed of only CB and PVDF with 50/50 weight percentage were also prepared for the indentation test.

Fig. 2 shows the scanning electron microscopy (SEM) images on the cathode microstructure consisting of nearly spherical NMC particles (estimated average diameter of approximately 10 μm) and a CB/PVDF porous matrix. Fig. 2(b) shows the magnified view on a single NMC532 particle which is closely packed by primary powders. The electrode thickness (excluding the Al current collector) ranges from 45 to 57 μm as shown in Fig. 2(c).