Probing the aging effects on nanomechanical properties of a LiFePO₄ cathode in a large format prismatic cell

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Abstract

Li-ion batteries offer great promise for the future of energy storage due to their superior gravimetric and volumetric energy density. One of the challenges in promoting their expanded use is to improve the cycle life of Li-ion batteries. This requires detailed understanding of the aging phenomenon. The aging mechanism of Li-ion batteries can have both chemical and mechanical origins. While the chemical degradation mechanisms have been studied extensively, mechanical degradation mechanisms have received little attention so far. In this study, we probe the changes in mechanical properties of a LiFePO₄ cathode in a large format prismatic cell. Results indicate that mechanical degradation increases by aging; in addition, local degradation is observed in the composite cathode. Implications of the degradation in mechanical properties on binder degradation are discussed in detail.

Keywords: Li-ion battery, mechanical properties, atomic force microscopy, nanoindentation, aging, prismatic LiFePO₄

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1. Introduction

The quest for a clean and renewable energy source is gaining momentum due to the urgent need to address global warming, reduce dependence on foreign oil, mitigate environmental pollution, and save the earth's limited oil reserves for future generations [1]. The transportation sector is responsible for 32% and 22% of the total CO₂ emission in US and worldwide, respectively [2, 3]. Therefore, gradual replacement of oil with a carbon free energy source in mobile platforms is essential to limit CO₂ emissions. Energy storage system requirements for mobile applications are especially challenging due to weight and space limitations in these platforms. The most notable energy storage media for mobile platforms are batteries [4], hydrogen [5], and bio-fuels [6]. Among these, batteries (i.e., nickel metal hydride, Toyota Prius) became popular by the introduction of hybrid electric (HE) vehicles [7]. Because of the demand for a longer range solely on electric power, plug-in hybrid (PHEV) and electric vehicles (EV) were developed. This resulted in the use of Li-ion batteries in PHEV and EV vehicles, since Li-ion batteries have superior gravimetric and volumetric energy density as compared to other battery chemistries [8].

Li-ion battery technology has made great strides since the 2000s; however, wider market penetration of EVs requires improvements in energy/power density, safety, cost, and cycle life of Li-ion batteries. In addition to mobile applications, Li-ion batteries are also considered for grid-scale stationary storage applications, which require a significant cycle life [9, 10]. Therefore, one of the challenges in promoting Li-ion batteries for energy storage applications is to improve their cycle life. This requires a detailed

understanding of the aging phenomenon [11-14]. Typical commercial electrodes are comprised of carbon coated active material and a binder [8]. The interplay between various battery subcomponents, such as cathode, anode, binder, separator, electrolyte, and current collector, determines the aging mechanism of Li-ion batteries. That aging mechanism can have both chemical and mechanical origins that are closely interrelated. Chemical degradation mechanisms have been studied extensively: solid electrolyte interphase formation [15], solvent co-intercalation [16], electrolyte decomposition and reduction [17, 18], gas evolution [19], active material dissolution [20], and loss of lithium [13] are the most notable ones. Mechanical degradation mechanisms are mostly associated with volume changes and stress generated during Li de/-intercalation in an active material (i.e., cathode or anode). As a result of volume changes and stress generated, active particles may form cracks, lose contact from each other or the current collector, and become isolated [21-23]. In addition, it was shown that stress generated during cycling of a battery alters the pore structure of a separator and results in lower Li ion mobility [24, 25].

Another important component of a battery is the binder, polyvinylidene fluoride (PVDF) being the most common one utilized in Li ion batteries. The binder keeps the active material together and in contact with the current collector, as well as providing a porous matrix for Li-ion mobility. It has to be electrochemically inert and should have desirable mechanical properties to accommodate volume changes in the active material and the corresponding stress generated during de/-lithiation [26]. Therefore, the binder should be elastic enough to accommodate the volume changes and should be able to adhere to the active material strongly. Despite the binder's considerable importance on

the performance of a Li-ion battery, degradation studies on the binder have received little attention so far [27, 28]. Chemical [29, 30] and mechanical [31] degradation of PVDF binder, as well as alternatives to the PVDF binder [32-36] have been reported previously. However, more work on binder degradation is required to better understand its magnitude on overall battery degradation, and to delineate its significance on stress related mechanical degradation, as explained below.

Isolation of the active particles has long been determined as one of the main causes of battery degradation [14]. From the foregoing narrative, we can identify three possible explanations for this phenomenon: (a) formation of cracks in an active material and eventual fragmentation (i.e., stress affecting active material, mechanical degradation), (b) fracture of the binder interconnecting active particles (i.e., stress affecting binder, mechanical degradation), and (c) deterioration of the adhesion properties of the binder (i.e., chemical degradation). Therefore, isolation of the active particles can have roots in mechanical degradation of the active material and binder, as well as chemical degradation of the binder. The root cause of active particle isolation is seldom discussed in the literature.

LiFePO_4 is one of the more promising Li-ion chemistries due to its high theoretical capacity, superior cycle life, thermal stability, and low cost [37]. A composite LiFePO_4 battery cathode is comprised of carbon coated active material and PVDF binder. LiFePO_4 particles are stiff and hard with a modulus of elasticity around 120 GPa, according to theoretical calculations [38]. On the other hand, PVDF binder is soft and compliant with a modulus of elasticity around 3 GPa [39]. Therefore, the active material of a composite cathode can be considered as floating in a PVDF binder matrix.

Nanoindentation is a powerful technique to measure the mechanical properties (i.e., modulus of elasticity and hardness) of materials at nanoscale [40]. Since composite electrodes are significantly thin ($< 100\text{ }\mu\text{m}$, $\approx 20\text{-}30\text{ }\mu\text{m}$ for high power applications) [41], nanoindentation is extremely useful to determine the mechanical properties of the composite electrodes. As explained previously, a LiFePO_4 composite cathode is comprised of carbon coated active material and PVDF binder, PVDF binder being the compliant component. Therefore, a nanoindentation experiment on a composite cathode results in the mechanical properties of the PVDF binder and not of the LiFePO_4 active material. Hence, it is possible to study the mechanical degradation of PVDF binder by probing the mechanical properties of a composite cathode.

Our aim in this study is to understand how aging affects the mechanical properties of a LiFePO_4 composite cathode in a prismatic cell, and, more specifically, the PVDF binder of the composite cathode. Three different cells aged at different conditions (see Table 1) were used to study the extent of the mechanical degradation of the PVDF binder. Atomic force microscopy (AFM) was used to probe the morphology, and a nanoindenter was used to probe mechanical properties of the composite cathode. Underlying reasons for PVDF binder degradation are discussed in detail. In addition, spatial variation of degradation in the composite cathode is also reported.

2. Experimental details

2.1. LiFePO_4 prismatic cells, sample extraction and cycling conditions

LiFePO_4 prismatic cells - thin cells in a rectangular configuration - with a nominal capacity around 18 Ah were used. (A123 Systems, Livonia, MI, USA). Cells are composed of 20 sheets of accordion-style folded electrodes. Cathode samples are

composed of carbon coated LiFePO_4 active material and PVDF binder, and LiFePO_4 has a crystalline structure as shown by Channagiri et al. [42]. All cathode samples (S1-4) were extracted and stored in an ultra-high purity (99.999 %) nitrogen filled glove box which has oxygen and moisture levels below 0.1 ppm. As will be discussed in the following sections, degradation in Li ion cells is not homogeneous. Therefore, it is important to take local degradation into account in sample preparation, and extract all samples from the same location for cross-sample comparison. Hence, all samples (S1-4) were extracted from the same location, L1 (see Figure 1). Additional samples were extracted from sample S4 at five different locations (L1-L5) to probe the local degradation as shown in Figure 1.

Cycling conditions of all cells are summarized in Table 1. An unaged cell, sample S1, was only cycled one time to ensure it was working properly and to determine its capacity. All other cells (S2-4) were cycled in an environmental chamber kept at 55°C. A relatively higher aging temperature was selected to accelerate aging experiments, as well as to facilitate probing the local degradation. All cells were charged at one C rate in constant current-constant voltage (CC-CV) mode regardless of the discharge rate. One C rate means that charging the entire battery will take one hour. Upper and lower cut-off voltages during charge and discharge were 3.6 and 2.0 V, respectively. Aging protocol was stopped once the cell capacity drop to 90% (S2 and S4) or 80% (S3) of its initial capacity.

2.2. Structural and morphological characterization

Morphology and surface roughness of the cathode samples were probed using an AFM (Agilent 5500, Chandler, AZ, USA). All AFM images were taken in contact mode

using a silicon probe (Agilent, PPP-CONT) with a force constant of 0.2 N/m and a resonant frequency of 13 kHz. An AFM scan speed of 1 Hz or slower was used to obtain an image with a 512 x 512 resolution or higher. AFM images were then post-processed using Gwyddion software.

2.3. Nanomechanical testing

The hardness and modulus of elasticity of the cathode samples were measured using a Triboscope probe based scanning nanoindenter head (Hysitron TS 75, Eden Prairie, MN, USA), which was attached to an AFM (Bruker Dimension 3100) with a diamond cono-spherical probe ($\sim 4 \mu\text{m}$ radius) [40]. Cono-Spherical probes are conical shaped probes with a spherical end. Cono-spherical probe was selected over Berkovich probe ($\sim 100 \text{ nm}$ radius) to obtain average value of the mechanical properties over a wide area (see section 3.2 for more details). Cono-spherical probe's surface area was calibrated using polycarbonate sample before measurements [43]. Nanoindentations were conducted in displacement control mode, and a maximum indentation depth of 1000 nm was used for each indent. The load was ramped in 5 s until the depth of 1000 nm was reached. Then, the load was kept constant for 2 s at this depth to observe any creep behavior. The load was then unloaded in 5 s. Around 10-15 indentations were performed at least $20 \mu\text{m}$ apart at different locations for each sample. The hardness (H) and modulus of elasticity (E) were calculated using the Oliver and Pharr method [44].

3. Results and discussion

In the following sections, first, morphology and surface roughness of the unaged and aged LiFePO_4 prismatic cell cathodes are presented. Then, degradation of the mechanical properties of the aged LiFePO_4 cathodes and its implications on PVDF binder

degradation are discussed in detail. Finally, local aging of a LiFePO_4 cathode in microscale, as evidenced by probing the mechanical properties at different locations, is presented.

3.1. Morphology of the cathode samples

Morphology and the surface roughness of the unaged (S1) and aged (S2-4) samples were investigated by AFM and results are shown in Figure 2. We did not observe significant changes in morphology or detected particle agglomeration in aged samples as compared to unaged sample. Average particle size is found to be around 250 nm. The unaged sample (S1) has the highest surface roughness, whereas the sample aged at the most severe conditions (S4) has the lowest surface roughness. All aged samples showed less surface roughness as compared to unaged sample.

3.2. Mechanical properties of the cathode samples

Mechanical properties of a composite cathode (i.e., hard active material dispersed in polymer matrix) is determined by several parameters: (a) properties of the polymer matrix (PVDF, dominant factor since it's the complaint component), (b) properties, size, and distribution of LiFePO_4 active material, (c) interfacial bonding, and (d) electrode manufacturing method (i.e., synthetic and processing) [45]. Since we acquired the LiFePO_4 prismatic cells from the same manufacturer, we can assume that the aforementioned parameters that control the mechanical properties of the composite cathode are similar in all samples. Considering the accuracy of the nanoindentation experiments on a composite cathode, another point that needs to be taken into account is the content of active material ($\approx 80\%$) and PVDF binder ($\approx 5 - 10\%$). During an actual indentation experiment, it is possible that the probe can first come in contact with the

active material. It could then push the active material into the polymer matrix or it could even push separate active materials into each other. All of these possibilities can affect the accuracy of the measurements. To circumvent this problem, we used a cono-spherical diamond probe (4 μm radius) instead of a Berkovich probe (100 nm radius). This gives us an average measurement over a wide area and minimizes local effects associated with using a probe with a small radius. Indeed, nanoindentation experiments conducted with a Berkovich probe resulted in much higher discrepancy compared to cono-spherical probe.

Modulus of elasticity and hardness of unaged and aged composite cathodes are given in Figure 3 and summarized in Table 2. Unaged cathode S1 showed the highest modulus of elasticity and hardness. As aging becomes more severe (i.e., S2 $\rightarrow$ S3), both modulus of elasticity and hardness decreased. In addition, S4 (i.e., sample cycled at 2C rate) showed the lowest modulus of elasticity and hardness, indicating that the effect of the C rate is more detrimental than the end of life capacity (i.e., S4 compared to S2 and S3) on mechanical properties.

With common preparation techniques, the degree of crystallinity of PVDF is around 50 % unless it is subject to a special treatment, such as electron beam radiation [46]. In addition, PVDF has four crystalline phases, α , β , γ , and δ . The α phase is the most common one [47]. In polymers, crystalline phase content is directly correlated with the hardness; as crystalline phase content decreases hardness of a polymer decreases [48, 49]. In addition, lithium salts (i.e., LiClO_4 , a common electrolyte utilized in Li-ion batteries) are shown to cause amorphization of the PVDF binder matrix [50]. Therefore, decreasing hardness of the LiFePO_4 composite cathode by aging as shown in Figure 3(b) can be considered as reduced crystallinity in the PVDF binder. Moreover, modulus of elasticity

also follows the same trend as hardness, and decreases by aging. It was shown that in some polymers (i.e., polyethylene), modulus of elasticity decreases with the degree of crystallinity [48, 51]. In summary, degradation of the mechanical properties of a composite cathode indicates that the crystallinity of the PVDF binder is decreasing by aging.

We further analyzed the local degradation of the composite cathode at five different locations (see Figure 1) extracted from sample S4. Spatial variation of the mechanical properties is shown in Figure 4 and summarized in Table 3. Local degradation of a composite cathode is also reported by others on both microscale [52-54] and macroscale [55], and can be ascribed to inhomogeneities in the composite cathode [56]. Unlike others [55], we did not observe a pattern in local degradation (i.e., edges being degraded more compared to center). However, one should note that, in this study, mechanical properties were probed from a small area ($\approx 100 \times 100 \mu\text{m}$) of sample S4; therefore, results indicate local degradation on microscale as opposed to macroscale.

4. Conclusions

In this study, we studied how aging affects the mechanical properties of a LiFePO_4 composite cathode by nanoindentation in a prismatic cell. Since PVDF binder is the compliant component of a LiFePO_4 composite cathode, the probed mechanical properties are associated with the PVDF binder. Three different cells aged at different conditions were utilized to study the extent of mechanical degradation of the PVDF binder. Results showed that both modulus of elasticity and hardness decrease by aging. The sample aged at 2C rate (i.e., S4) showed the highest degradation in modulus of elasticity and hardness, indicating that the effect of the C rate is more prominent than the

end of life capacity on mechanical degradation. Degraded mechanical properties of the PVDF binder is considered to be associated with the reduced degree of crystallinity of the PVDF binder. Moreover, we observed local degradation in the composite cathode by probing the mechanical properties of the samples that are extracted from five different locations, indicating inhomogeneous degradation at the microscale.

Further work is necessary to understand the changes in the structure of the PVDF binder. Fourier transform infrared spectroscopy can be utilized to determine the changes in crystalline structure of the PVDF binder. Moreover, probing the mechanical properties of the LiFePO_4 active particles (i.e., after removing the PVDF binder with an appropriate solvent) that are extracted from the composite cathode can reveal additional information on the main cause of degradation in the mechanical properties of a composite cathode.

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Table 1. Cycling rate, cycling temperature, end of life capacity, and number of cycles of A123 prismatic LiFePO₄ cells.

Sample #	Discharge rate (C rate)	Temperature (°C)	End of life capacity (%)	Number of cycles
S1 (unaged)	–	–	100	–
S2	1	55	90	459
S3	1	55	80	517
S4	2	55	90	171

Table 2. Mechanical properties of all samples.

	Composite cathode samples aged at different conditions			
Mechanical Property	S1 (unaged)	S2	S3	S4
Modulus of elasticity (GPa)	8.42 ± 0.87	6.45 ± 0.68	4.94 ± 0.39	2.01 ± 0.32
Hardness (MPa)	279.5 ± 31.4	226.3 ± 21.1	182.9 ± 21.2	107.8 ± 16.5

Table 3. Spatial variation of the mechanical properties of sample 4.

	Locations of the samples extracted from sample S4				
Mechanical Property	L1	L2	L3	L4	L5
Modulus of elasticity (GPa)	4.94 ± 0.39	3.83 ± 0.32	2.84 ± 0.27	1.94 ± 0.25	2.25 ± 0.26
Hardness (MPa)	182.9 ± 21.2	154.9 ± 11.9	134.5 ± 14.1	130.5 ± 13.1	108.9 ± 10.4

Figure captions

Figure 1. A123 prismatic cell cathode, LiFePO_4 . All samples (S1-4) were extracted from location L1. Additional samples were extracted from sample S4 at five different locations (L1-5) to probe local degradation.

Figure 2. AFM images of unaged sample and samples aged at different conditions, (a), (b), (c) and (d) corresponds to samples 1, 2, 3 and 4, respectively; refer to Table 1 for aging conditions.

Figure 3. Modulus of elasticity (a) and hardness (b) of unaged sample (S1) and samples aged at different conditions (S2-4).

Figure 4. Modulus of elasticity (a) and hardness (b) of samples extracted from different locations of sample 3.