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Strain and Conductivity in Lithium Ion Battery Binders

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Introduction

Lithium batteries provide high energy density storage with applications ranging from consumer electronics to electric vehicles. However, they have a limited lifespan and experience capacity loss with aging. Multiple mechanisms contribute to battery aging. The battery binder plays two important roles in the electrodes, and the damage it sustains during cycling may play a role in the degradation of the overall battery performance. Mechanical stress during battery operations occurs as a result of the swelling and shrinking of the electrodes because of the movement of lithium with cycling. The yield stress of the swollen polyvinylidene fluoride carbon black (PVDFCB) binder was measured at approximately 4MPa for PVDF with carbon black CB weight fractions between 10-30% swollen in propylene carbonate. This is far less stress than is typically experienced in an electrode during cycling. The effects of this permanent damage to the binder were explored by measuring the conductivity loss with strains in excess of the binder yield.

Lithium-ion battery binder is a composite material consisting of a polymer embedded with conductive carbon. PVDF is the most commonly used polymer in Li-ion battery binder. The polymer component holds the electrode together, but is electrically insulating and therefore relies on the conductive carbon particles to form electron pathways through the binder. The conductivity of the binder is dependent on the weight fraction of conductive particles. Multiple experiments have explored this relationship. Liu examined binder conductivity as a function of the weight-percent conductive carbon. At around 20wt%AB, the conductive network is percolated. The conductivity is low below this point and increases rapidly until 20wt%. At carbon fractions greater than 20wt%, conductivity increases at a slower rate [1].

The PVDFCB binder experiences numerous mechanical stresses both during manufacturing and throughout the battery's lifetime. The modulus of dry PVDF is an order of magnitude greater than when it is swollen in the battery electrolyte solvent. The binder faces potential damage while in both states. While in its dry state, PVDFCB undergoes manufacturing stresses such as calendaring to reduce porosity and thickness. This mechanically stresses the binder when it is in its dry, stiffer state. During battery operation the binder is maintained in battery electrolyte. The binder absorbs some of this, increasing slightly in size and decreasing in modulus. The binder is in this softened state as the battery cycles and experiences the mechanical stresses induced by the volumetric changes.

Commercially available lithium-ion battery electrodes with graphite:$LiCoO_2$ chemistries undergo small volumetric changes of less than 10% during lithiation and delithiation [2]. As lithium enters or exits the structure, the electrode changes in volume to accommodate. Other possible anode active materials are being explored. Both silicon and tin could potentially provide higher capacities than graphite. However, insertion of lithium into the structure results in a 310% and 260% volumetric expansion for silicon and tin respectively [4]. Large volumetric change is a major obstacle to these new materials as it damages the electrode and can significantly decrease the battery lifespan.

Low Strain Amplitude Testing

Testing at low strains examines binder behavior prior to yielding and permanent damage. Cycling repeatedly stresses the PVDFCB binder as it conforms to volumetric changes of the electrode. Electrodes are composite, non-uniform structures, and, as such, electrode stress profiles during cycling are non-uniform as well. The behavior of PVDFCB binder in lower stress areas can be explored by looking at the response of PVDFCB to low strains. Higher stresses, resulting in permanent damage, are discussed in the next section.

To conduct this testing, rectangular samples of PVDFCB binder were oscillated on the Netzsch Dynamic Mechanical Analyzer to determine the amplitude dependency of the modulus. Amplitude testing explored the strain hardening behavior of PVDFCB at low strains. The initial sample length of was 5mm and the oscillation amplitude was varied from 1um to 240um.

The DMA cycled at 1Hz for three minutes at each given amplitude. During that time both the strain and modulus were measured. As seen in Figure 1, the modulus increases with amplitude/strain until it reaches a maximum strength. Dry PVDF with carbon black fractions between 0wt%CB to 40wt%CB were tested. The 35wt%CB and 40wt%CB experienced a maximum modulus at 16um amplitude, while the remaining dry samples had a peak modulus at 32um. A 20wt%CB sample of swollen PVDFCB was tested to examine the differences between dry and swollen PVDFCB binder behavior at small strains. The swollen sample experienced only a small increase in modulus compared to the dry samples whose moduli increased 100s of MPa.

After reaching peak strength, most samples experienced a decrease in modulus. The dry PVDFCB samples were unable to endure high strains without failure and tearing. Once the samples tore, the DMA aborted the remainder of the run. The 20wt%CB and 35wt%CB were able to withstand all amplitudes in the testing range, while the other weight fractions failed at either 32um or 64um amplitudes.

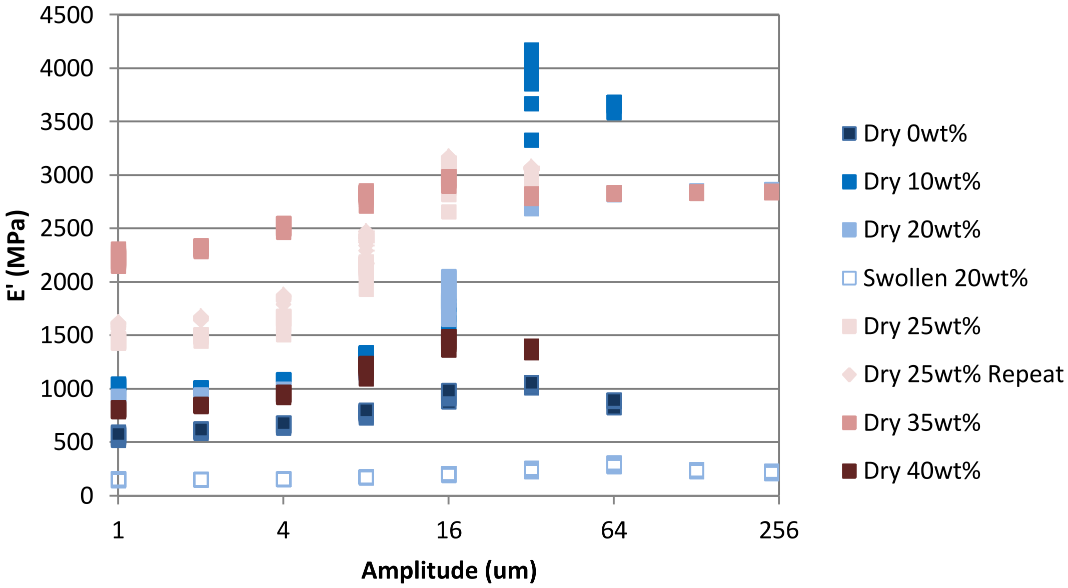

Figure 1. Modulus Change in PVDFCB with Variation of Oscillation Amplitude

Yield Stress

During both manufacturing processes and throughout the battery lifetime, the binder experiences mechanical stresses. Electrode swelling during cycling causes the binder to strain in response to volumetric changes. This is a non-uniform process and can result in localized high-stress regions. According to modeling of the $LiCoO_2$ cathode by Mendoza, peak stresses in the cathode can reach 9GPa. The binder, which has a lower modulus than the active materials, serves to reduce this stress; however, even with binder present, cathode stresses can reach 100's of MPa [5].

The Netzsch DMA in tensile mode was used to determine the yield point of the PVDFCB binder. A rectangular sample of binder film was cut and then trimmed using a 3/16" diameter punch. Both dry samples and samples that had been swollen in propylene carbonate overnight were tested. The testing design consisted of steps in which a sample was ramped to the maximum step force for three minutes and then dropped to 0N for two minutes. The dry samples were ramped from maximum forces of 1N to 12N in 1N increments, while the swollen samples were ramped from 0.25N to 3N. An example step from a swollen PVDFCB sample is shown in Figure 2, highlighting both the elastic and yielded regions. The values of force on the left axis are negative because it was a tensile force.

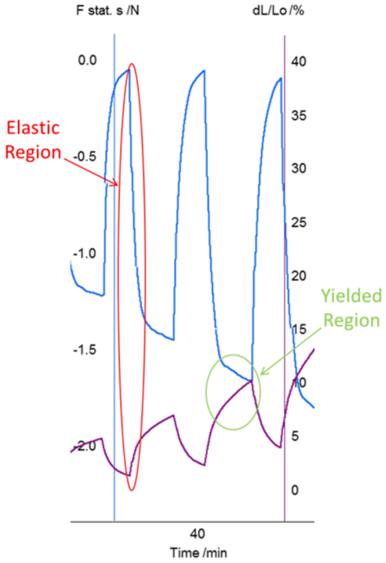

Figure 2. View of Swollen Yield Stress Experiment from DMA with Elastic and Yielded Regions of a Step Indicated

Although the yield stress shows a carbon black dependence in the dry binder samples as seen in Figure 3, the swollen samples yielded at approximately the same stress, around 4MPa, regardless of carbon black content. Yield point plays an important role because the binder conductivity is dependent upon the conductive carbon particles staying in contact to form a network. Plastic deformation that the PVDFCB binder undergoes after yielding permanently increases the distance between these particles. During cycling, stresses in excess of the binder's yield strength occur, which could potentially permanently damage the binder's conductive properties. This is examined in further detail in the following section.

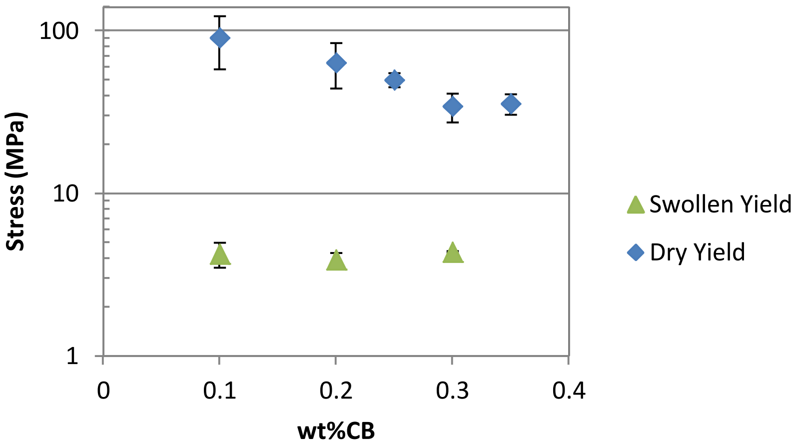

Figure 3. Swollen and Dry PVDFCB Binder Yield Stress

The behavior after yielding also differs between swollen and dry PVDFCB. The dry PVDFCB was tested at 10, 20, 25, 30, and 35wt%CB; while the swollen PVDFCB was tested at 10, 20, and 30wt%CB. The test run was not stopped after the sample yielded, but continued until the maximum force had been reached or the run had failed. After yielding the dry samples were only capable of sustaining an additional 0.8-2.2% strain before catastrophically failing and tearing. The morphology change associated with catastrophic failure can be seen in the SEM images in Figure 4, showing dry PVDFCB with 30wt%CB before and after tearing. The post-strain image on the right shows that the PVDF has been orientated in the direction of tension and pulled into long strands, separating the carbon black particles. During the SEM imaging process, charge build-up was evident on the strained portion of the sample. Binder with 30wt%CB is normally conductive, so a charge build-up on the failed sample was indicative that straining the PVDFCB binder interfered with its conductive properties. The image after failure shows that the distance between carbon black particles has increased dramatically to the point where they are no longer capable of forming a conductive network. The ultimate strain at failure (the point at which the sample tore) for dry PVDFCB was 6.9±2.2%strain for 10wt%CB and decreased with increasing carbon black content with the highest weight fraction tested, 35wt%CB, failing at 3.5±0.4%strain.

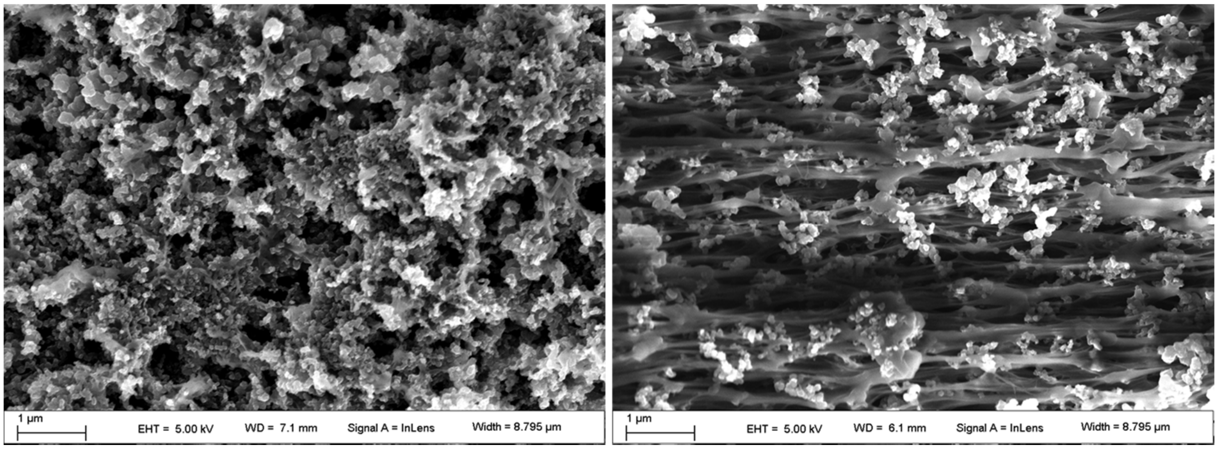

Figure 4. SEM images of Dry PVDF with 30wt%CB Before and After Catastrophic Failure

The swollen samples behaved differently and experienced a large period of plastic deformation post yield. The swollen samples yielded at strains less than 5%. Efforts to determine at what point the swollen samples experienced catastrophic failure and tore were unsuccessful. Initial testing on swollen 20wt%CB showed the samples were able to reach strains in excess of 100%. The DMA was unable to accommodate changes in strain of that magnitude in the testing mode used for this experiment, so the tearing point was unable to be determined. However, it provided evidence that dry and swollen samples failed in different manners. The dry PVDFCB binder fails catastrophically shortly after yielding, while the swollen binder experiences a large period of plastic deformation after yield. This deformation, though it doesn't physically tear the binder, is responsible for damaging the conductive properties of the binder.

Conductivity Change with Strain

The active material of the cathode, $LiCoO_2$, is less conductive than the PVDFCB binder. As such, the binder plays an important role in enhancing the electrode electrical conductivity. The conductivity of 10wt%CB, 20wt%CB, and 30wt%CB binder films swollen in propylene carbonate were tested at strains of 0% 10%, 40%, 80%, and 100%. The stress needed to achieve each of these strains was between 9-16MPa, indicating all samples had experienced enough stress to yield. These stresses are also all less than those predicted to be seen in cathodes during cycling [5]; stress conditions endured during this testing could feasibly occur during typical battery cycling.

To explore the relationship between conductivity and strain, rectangular samples of PVDFCB were cut from films and then soaked in propylene carbonate for at least 24 hours before use. The DMA was used in tensile mode and was set to ramp to a pre-defined strain, while the sample was held in a propylene carbonate bath. The resistance was measured using a FLUKE 87 III True RMS Multimeter over a 5mm section of sample before and after straining. These along with the cross-sectional area were used to calculate sample conductivities. The average strain rate with 95%-confidence interval for 40%, 80%, and 100% strains was 33.8±0.7% strain per minute; while the 10% strain had an average strain rate of 17.4±2.3% strain per minute. The DMA's strain rate could not be directly defined, resulting in this difference. Additionally, the strain rate was not constant, and the DMA decreased the rate as the sample strain approached the set strain.

The left chart in Figure 5 shows the conductivity change with strain. Increasing strain further separates carbon black particles, disrupting the network and resulting in a loss of electrical conductivity. The right chart in Figure 5 shows the conductivity as a function of vol%void space. As carbon black content is increased in PVDFCB binder, there is a rapid increase in electrical conductivity during the formation of a percolated network. After the network is fully formed, increases in conductivity are more modest. The rapid decrease in electrical conductivity with increase of void space is the inverse of this process. As the vol% of void space increases, the rate of decrease in conductivity accelerates, indicating that a percolated network no longer exists.

The samples' gap between the crosshead bars of the DMA was a constant 5mm, giving all samples the same initial length. The cross-sectional areas of the 20wt%CB binder samples were measured before and after strains ranging from 10% to 100%. No visible necking was apparent after strain and the average cross-sectional area after strain was 98.7%±0.7% of the original cross-sectional area for the 20wt%CB binder. This was the intermediary carbon black fraction tested and it is assumed area change was similar for the other carbon black contents tested. The near constant cross-sectional area despite an increase in length indicates that straining the binder resulted in increased binder porosity. Larger pore space increases the distance by which carbon black particles are separated, hindering their ability to conduct electrons. Initially PVDFCB binder is approximately 40%vol void space. Assuming no change in the cross-sectional area, the void space increases to an average of about 45%vol at 10%strain and 70%vol at 100%strain.

During battery operation, this void space is filled with battery electrolyte. Since electron flow is primarily through the conductive carbon and active materials, this signifies an increase in the non-conductive portion. As more void space is created, the conductive electrode components are separated. Through this mechanism conductive materials can be isolated and removed from the conductive network. Electrons travel through a continuous conductive network. As the amount of material within the network is decreased by particles becoming isolated, the number of electron pathways is diminished and the electrical conductivity drops in response. Initially, both the 20wt% and 30wt%CB binders form percolated networks. The void space is a non-conductive element and additional void space reduces the ability of electrons to move through the binder. When enough void space has been added to the PVDFCB binder that the carbon black no longer forms a percolated network, the decrease in conductivity accelerates. This pattern of conductivity loss is characteristic of the disruption of a percolated network. The 10wt%CB binder sample was below the percolation threshold, so there wasn't a percolated network to disrupt, resulting in the different pattern of conductivity loss.

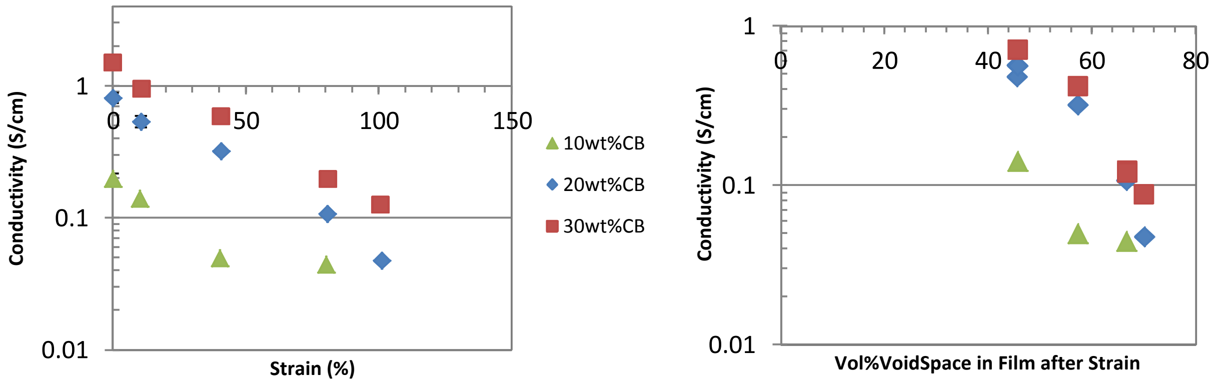

Figure 5. Conductivity of Swollen PVDFCB Binder as a Function of Strain (Left) and Corresponding Vol% Void Space (Right)

The SEM images in Figure 6 show the morphology change that occurs with strain in the swollen 30wt%CB samples. These were all swollen samples, strained in propylene carbonate, and then vacuum dried overnight before imaging. The two images in the top row show samples strained to 10% and the three in the bottom row were strained to 100%. These are both strains greater than the strain at yield for swollen PVDF with 30wt%CB, which means they've experienced some plastic damage. The damage sustained by these samples looks different than the catastrophic failure shown in the images of the dry 30wt%CB PVDF binder in Figure 4. The polymer is more visible in both the 10%strain and 100%strain samples than in the completely unstrained SEM image shown previously in Figure 4. However, the polymer has not been pulled into long strands. The 100%strain shows more variability in morphology with some regions such as those on the bottom left and center showing large areas of polymer, while others such as those on the bottom right closely resembling the 10%strain images. During catastrophic failure, the entire region became non-conductive leading to charge build-up during imaging. The non-uniform plastic failure seen in Figure 6 shows regions in which the carbon black particles have been separated by polymer, while they remain in contact in other areas. This incomplete failure leads to a decrease in PVDFCB binder conductivity without it becoming completely non-conductive.

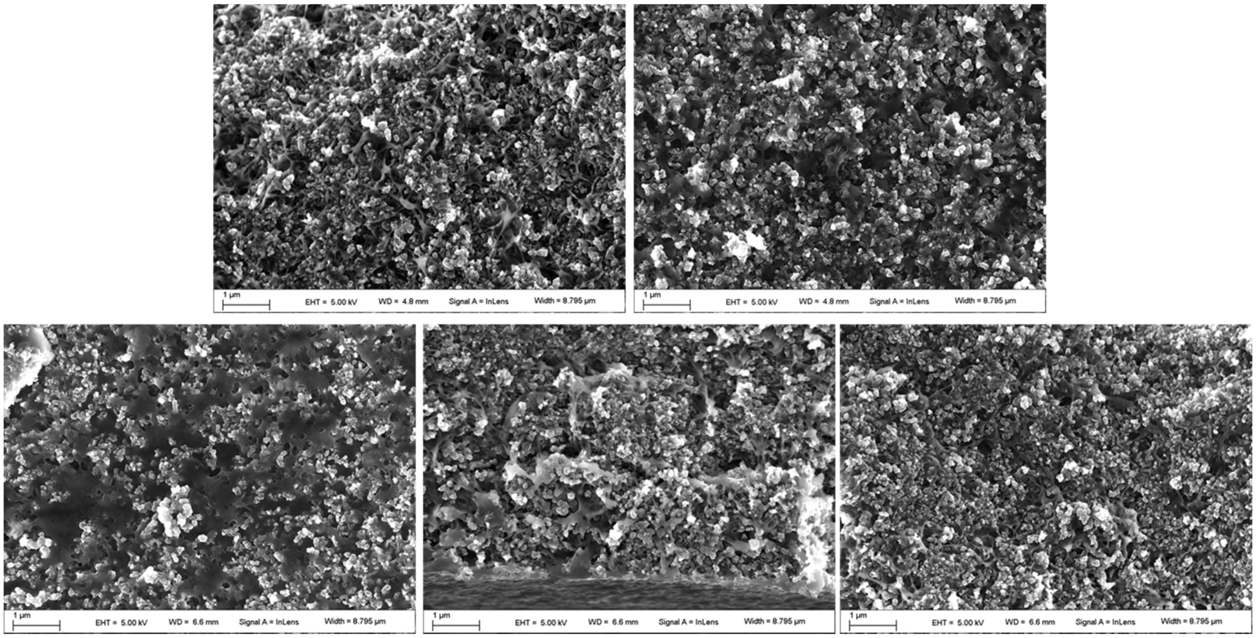

Figure 6. The top row shows SEM images of the PVDF with 30wt%CB swollen in propylene carbonate after being strained to 10%, and the bottom row shows SEM images of a samplestrained to 100%. The samples were strained while held in propylene carbonate and subsequently vacuum dried before imaging.

PVDF is electrically insulating, so electrons travel along a path of carbon black. As these particles become separated further the network is no longer continuous, reducing the number of pathways electrons can travel through the binder and lowering the conductivity. Since the binder conductivity is greater than the electrode active material's conductivity, a reduction in the binder conductivity should reduce the overall electrode conductivity.

Conclusion

The stresses in the cathode during cycling are greater than the PVDFCB binder's yield stress. As a result, repeated cycling may plastically deform regions within the swollen binder. This is a different damage mechanism than the catastrophic failure the dry PVDFCB binder experiences. The binder conductivity is dependent on a percolated carbon black network; damaging this network by permanently straining the binder and separating the carbon particles decreases binder conductivity. The binder conductivity is greater than the active material's conductivity, so a decrease in the binder conductivity should result in a decrease in the overall battery conductivity.

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