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Understanding the Mechanical and Electrochemical Impact of Binder Systems on Silicon Anodes in Lithium-Ion Batteries

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Abstract

Silicon has emerged as a promising alternative to traditional graphite as an anode material in battery technology, primarily due to its high theoretical capacity and abundance. However, its application is hindered by significant challenges, including severe volume expansion in the active material (~275%) during cycling, which can lead to a series of electrode failure issues. Polymer binder plays an essential role in addressing these challenges as it accommodates silicon's volume expansion and the rearrangement of particles. This work conducted an analysis of how different binders influence mechanical and electrochemical properties of silicon electrodes. Our findings are supported by a series of experiments, aimed at addressing the challenge of silicon volume expansion and improving the durability and efficiency of silicon-based anodes.

Water-soluble polyacrylic acid (PAA) has emerged as a promising binder material for silicon anodes, with lithium hydroxide (LiOH) frequently added to improve the rheological properties of the slurry. However, literature presents varying results regarding the electrochemical performance of batteries incorporating LiOH in PAA binders. In addressing these discrepancies, our research investigates the role of LiOH in PAA, defining its impact through two primary factors: lithium-ion concentration and pH level. Our analysis involved conducting cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests, which confirmed our hypothesis that the addition of Li^+ ions improves ion transport. Regarding pH, an optimal middle-ground pH level is identified, balancing the advantages shown at both lower and higher pH ranges.

Despite the observed benefits of water-soluble PAA binder, such binders frequently result in uneven carbon distribution in coating, attributed to the poor wettability of nano-carbon in water. Consequently, the next portion of this work revisits the use of a traditional NMP (N-Methyl-2-pyrrolidone) soluble binder, PVDF (polyvinylidene fluoride), known for its widespread application in battery technology. However, PVDF-based silicon anodes often exhibit poor cycling performance. To address this issue and enhance the binder's flexibility, we attempted to chemically modify PVDF by incorporating carboxylic acid ($-\text{COOH}$) groups and reducing the polymer chain length. Despite these efforts, the experimental results did not show an improvement in cycling performance. The findings suggest that the deteriorated performance may be due to a weakened adhesion to the current collector for short-chain polymers.

We then explore additional binder systems in an attempt to improve Si electrode performance. Our previous research suggests a trade-off between flexibility and adhesion in shortened polymers. To further verify this, we investigate the effect of two commercially available short-chain polymer binders, namely Jeffamine D-2000 and PAA(2000). Next, in order to mitigate the adverse effects of short polymer chain lengths on mechanical performance, we adopt an adhesion layer between the bulk electrode layer and the current collector. Finally, we evaluate several binders known for their promising results in other battery systems, including polyacrylonitrile (PAN), polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), and polyimide (PI). A series of mechanical and electrochemical characteristics of the as-mentioned binders are investigated. The findings confirm that shorter polymer chain length leads to a weaker adhesion between the electrode coating and the current collector. Additionally, we discovered that introducing an adhesion layer can enhance the cycling stability of silicon anodes.

Keywords: Li-ion battery, silicon anode, polymer, binder, chain length

4 Evaluating the Performance of Alternative Binders for Silicon Anodes

4.1 Introduction

In the previous chapters, we investigated modifications to PAA and PVDF binders to be used in silicon anodes. In the case of the modified PVDF, one potential cause of the reduced capacity could be the heterogeneous products of the modification reactions, which likely contributed to the poor results. Additionally, compromised adhesion between the bulk coating and the copper current collector, potentially resulting from the shortened polymer chain length, could have been another factor.

In this chapter, we explore three more binder performance issues. We first use commercial short-chain PAA and Jeffamine binders to investigate the chain-length effect and to assure the chemical uniformity of the binders. We also evaluate the performance of several novel binders that showed potential in other battery systems. Finally, we adopt an adhesion layer between the bulk electrode layer and current collector to mitigate the adverse effects of short polymer chain lengths on mechanical performance. Through these investigations, we aim to gain more insight into the effect of polymer chain length and functional groups on silicon anodes without sacrificing its adhesion ability.

The following binders were used in this study. We selected commercial polyacrylic acid (PAA) and Jeffamine D-2000, both of which have an average molecular weight of 2000. Additionally, we investigated polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), polyacrylonitrile (PAN), and polyimide (PI).

PAA (as shown in Figure 4.1) is one of the most widely used binder for high-capacity silicon anodes. Prior work has claimed an optimal molecular weight between 250 ~ 1250 kDa for cell performance, as we mentioned in the previous chapter [52, 54, 70, 71]. However, molecular weights below this range have not yet been explored. In part of this chapter, we focus on analyzing PAA with a significantly lower molecular weight, approximately 2000 Da, to evaluate its impact on both mechanical and electrochemical performance. This investigation helps us to answer the question of polymer binder chain length effect on cell performance.

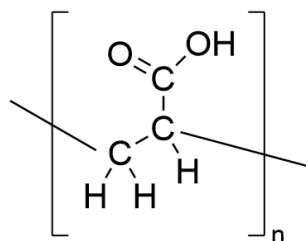


Figure 4.1: Molecular structure of PAA.

Jeffamine binders refer to the class of polyether amines (PEAs), which are polymers characterized by repeating ether linkages (-O-) and amine groups (-NH₂) in their structure (as shown in Figure 4.2). It has demonstrated desirable performance in various applications including polymer electrolytes and LiFePO₄ cathode binders in mechanical flexibility and environmental sustainability [72]. The flexibility of Jeffamine's backbone is primarily due to its ether linkages, which facilitate rotational freedom within the polymer chain, thereby reducing intermolecular forces and lowering its glass transition temperature [73]. However, research on utilizing Jeffamine as a binder in silicon anodes has not been performed to our knowledge. This exploration is driven by the hypothesis that Jeffamine's flexible backbone might effectively accommodate the volume changes that silicon experiences during cycling.

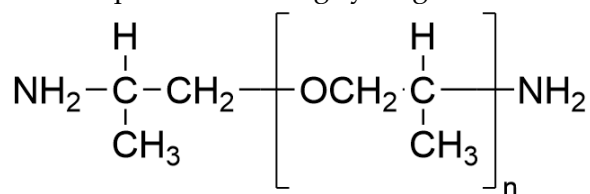


Figure 4.2: Molecular structure of Jeffamine.

PVDF-HFP is a copolymer composed of vinylidene fluoride and hexafluoropropylene as shown in Figure 4.3. Various research has been done to understand its functions in graphite, Li-O₂, LFP, and aqueous zinc-manganese batteries, though its application in silicon anodes remains unexplored. The presence of HFP within the PVDF polymer backbone introduces irregularities and decreases the crystallinity of the material. This structural modification reduces the interactions between polymer chains, making them easier to mobilize under thermal stress [74]. According to Ma et al.'s work, PVDF-HFP exhibits a reduced charge transfer resistance and suppressed the electrode surface cracks compared to tradition PVDF [75]. Building on these qualities, we study how PVDF-HFP performs in silicon anodes, potentially addressing the limitations of PVDF performance from the previous chapter.

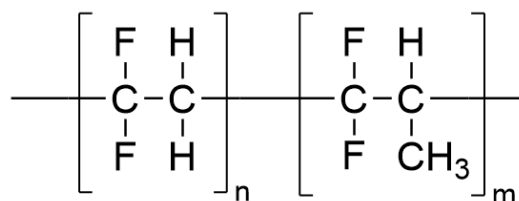


Figure 4.3: Molecular structure of PVDF-HFP.

PAN is characterized by its functional nitrile groups (as shown in Figure 4.4). Studies have shown that these groups contribute to enhanced ionic conductivity, increased adhesion strength, and reduced capacity loss due to its strong polarity from electronegative nitrogen [76, 77]. However, PAN's high glass transition temperature could also result in increased hardness and stiffness, potentially detrimental to silicon anodes' performance. Existing research has mostly focused on the slow-rate cycling performance of silicon anodes using PAN, where it demonstrated superior performance compared to PVDF [76]. Based on these observations, we argue that conducting more extensive C-rate testing would provide a deeper understanding of PAN's working mechanisms in silicon anodes.

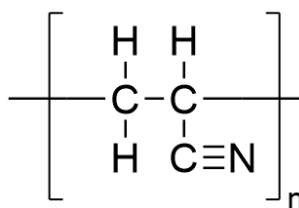


Figure 4.4: Molecular structure of PAN.

Polyimide (PI) binders, as shown in Figure 4.5, present a robust solution for silicon anodes in lithium-ion batteries, offering enhanced mechanical strength and stability [78-80]. This is particularly beneficial in accommodating the volume expansion and contraction of silicon during cycling [81]. However, the use of PI binders comes with its own challenges. Their higher production costs and the complexity associated with processing such materials pose considerable hurdles for manufacturing. In this study, we aim to assess the functionality of PI binders within silicon anodes, serving as a reference for other kinds of binders used in this chapter.

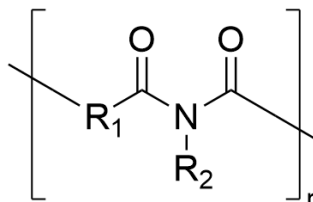


Figure 4.5: Molecular structure of PI.

While shortening the polymer chain increases the flexibility of the binder matrix, which can benefit the movement of silicon particles, it might reduce the adhesion between the coating layer and the current collector. To keep the benefits while mitigating the drawbacks, an adhesion layer can be introduced between the bulk material and the current collector, as is shown in Figure 4.6. This adhesion layer is composed of long-chain polymer binders and carbon black to enhance adhesion while also maintaining electrical conductivity.

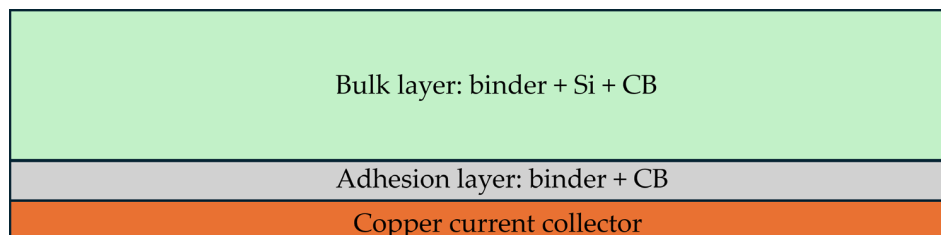


Figure 4.6: Cross-sectional demonstration of an adhesion layer between the bulk and copper.

Table 4.1 lists three major parameters for the binders that are tested in this chapter. Glass transition point is the temperature at which a polymer transitions from a hard, glassy state to a soft, rubbery state. For example, at temperatures below the glass transition point, the polymer chains are in a rigid state, exhibiting very limited mobility. In this state, the material is rigid and brittle because the molecular chains are locked in place, preventing them from sliding past one another. This lack of mobility contributes to the stiffness and brittleness of the material. Similarly, the melting point of a binder is essential for determining its thermal processing capabilities and ensuring operational stability, as it marks the temperature at which the binder transitions from solid to liquid, impacting the material's structural integrity and safety under operational conditions.

Table 4.1: Thermo and chemical properties of different binders.

Binder	Glass transition point (°C)	Melting point (°C)	Molecular weight (kDa)
PAA(2000)	103	116	2
Jeffamine	below room T	38	2
PVDF-HFP	-35	143	400
PAN	95	300	70
PI	300	350	500

The remainder of this chapter evaluates both electrochemical and mechanical performance of the binders. The cycling performance was measured on all the binders mentioned. A peeling test was performed to give insights on the cycling behavior.

4.2 Experimental and Materials

This part describes the experimental methods, equipment, and materials used.

Materials and Equipment

Carbon black (C45) was obtained from Timcal. Silicon nanoparticles (~100 nm) were purchased from Nanostructured & Amorphous Materials, Inc. PAN, PVDF-HFP, Jeffamine D-2000, PAA(2000), and NMP was acquired from Sigma-Aldrich. PI binder was offered by Argonne National Lab. Electrolyte (1.0 M LiPF₆ in EC and DEC with a volume ratio of 50:50) and additive fluoroethylene carbonate (FEC) were purchased from Sigma-Aldrich. Electrochemical tests were conducted using a Maccor 4300 battery tester.

Electrode Preparation

The fabricated silicon electrodes were composed of 60 wt.% silicon, 30 wt.% binder, and 10 wt.% C45. To prepare the binder solutions, each binder was gradually added to NMP or deionized water and mixed using a stir plate for 6 hours at approximately 22°C. The container was covered with a lid. Meanwhile, silicon and carbon black were ground in a mortar and pestle for 20 minutes. The binder solution and ground particles were then mixed in a sealed jar using a high-speed rotating homogenizer (Algimax GX 300) for 24 seconds. For the coating process, a 7 cm × 9 cm copper sheet was first cleaned using isopropyl alcohol. The electrode slurry was then coated on the copper sheet using a bar-type coating applicator with a 75 μm thickness side. The anode was subsequently dried in an oven at 100°C for 6 hours and calendered to achieve a 50% porosity. To improve the adhesion between the bulk electrode and the copper current collector, the PAA on PVDF series current collector was sanded with 600-grit sandpaper. This was followed by a treatment with 10 wt.% oxalic acid to remove any potential copper oxide layers.

Peeling Test

Peeling tests were conducted to evaluate the electrode integrity using an Instron 3343 stress-strain tester to evaluate the adhesion/cohesion of the binders. The laminate side of the electrode, measuring 30 mm × 54 mm, was attached to a strip of 2 cm wide aluminum-backed adhesive tape. The electrode portion underneath the adhesive tape was removed from its

current collector by pulling the tape at constant displacement rate of 500 mm/min as described more fully in Ref. [40]. The applied force was measured, and load/displacement plots were generated to analyze the results.

Cell Assembly and Electrochemical Characterization

Half cells were assembled using a silicon composite electrode as the working electrode, a lithium metal counter electrode, a microporous polypropylene separator (Celgard 2325) and 1.0 M LiPF₆ in EC:DEC:FEC (45:45:10 by volume) electrolyte. All cells were allowed to soak in the electrolyte overnight to ensure thorough penetration of the electrodes. Each cell then underwent 3 formation cycles at C/20 rate, followed by 4 lithiation cycles each at C/10, C/5, C/3, 1C and 2C rates and delithiation rate at C/3. The voltage window is from 0.05 to 1.5 V. The sequence of cycles is then repeated a second time, for a total of 44 cycles. All electrochemical measurements were conducted at 22°C.

4.3 Results and Discussion

4.3.1 Cycling results

For the rest of this chapter, we refer to half-cells by their binder types. For instance, “PI” means a cell using polyimide binder. Furthermore, for cells that insert an adhesion layer, we designate them as “A on B,” where “A” indicates the binders in the bulk layer and “B” refers to the binder in the adhesion layer. The number in “PAA(2000)” and “Jeffamine D-2000” specifies the average molecular weight of the binder.

Figure 4.7 shows the capacity of silicon anode half-cells using different polymer binders. Among these, PI demonstrates superior performance, maintaining the highest capacity. Notably, PVDF-HFP and short-chain polymer PAA(2000) and Jeffamine D-2000 show significantly lower capacities than PI, which may be related to the poorer adhesion properties which leads to ineffective electronic transport between the current collector and the coating. In addition, PAN displays high initial capacities but undergoes a rapid decline as the C-rate increases. This decline could be attributed to its low molecular weight (70 kDa) leading to a poor adhesion to the current collector. It is also possible that due to the mechanical stiffness, PAN cannot accommodate the volume changes of the silicon during cycling.

To evaluate the impact of adhesion, we tested a mixture of long-chain and short-chain PAA at a 1:1 weight ratio, applied with and without an adhesion layer.

Figure 4.7 shows that PAA(2000) + PAA exhibits excellent initial capacities that is higher than pristine PAA. When combining short and long chain PAA together, it may offer a synergistic effect where this combination takes the advantages of flexibility from PAA(2000) and the adhesion capacity from PAA. However, PAA(2000) + PAA shows a dramatic capacity drop as the C-rate increases. It could be due to the weak adhesion between the bulk and the copper, as we further confirmed in the peeling test.

On the other hand, the PAA(2000) + PAA on PAA cell maintains a more stable capacity performance throughout all the C-rates, though its average capacity is lower than that of PAA(2000) + PAA.

The lower capacity of PAA(2000) + PAA on PAA could be attributed to its manufacturing process. As shown in Figure 4.6, an adhesion layer consisting of PAA and carbon black in water was applied to the copper surface. This layer was then dried at 100°C for 3 hours to eliminate any liquid residual. Subsequently, a bulk electrode layer comprising PAA, silicon, and carbon black in water was coated on the top of the adhesion layer. This electrode was further dried in an oven at 100°C for 6 hours and was then ready for use. A challenge arises when the water-soluble bulk layer is coated on the similarly soluble adhesion layer, leading to blending of the two layers. This blending can compromise the homogeneity and integrity of both layers, potentially increasing susceptibility to delamination and adversely affecting the electronic pathways.

In order to overcome the undesired blending between adhesion and bulk layers, we modified our method by formulating an adhesion layer using PVDF binder dissolved in NMP. PVDF is not soluble in water, so when the subsequent PAA-based layer is added to the adhesion layer, very little blending will occur. The cycling results show that with this new adhesion layer, PAA(2000) + PAA on PVDF does show an improved average capacity (around 500 mAh/g higher) compared to that of PAA(2000) + PAA on PAA. In fact, at high rates of lithiation, this formulation outperforms all the others observed in this study.

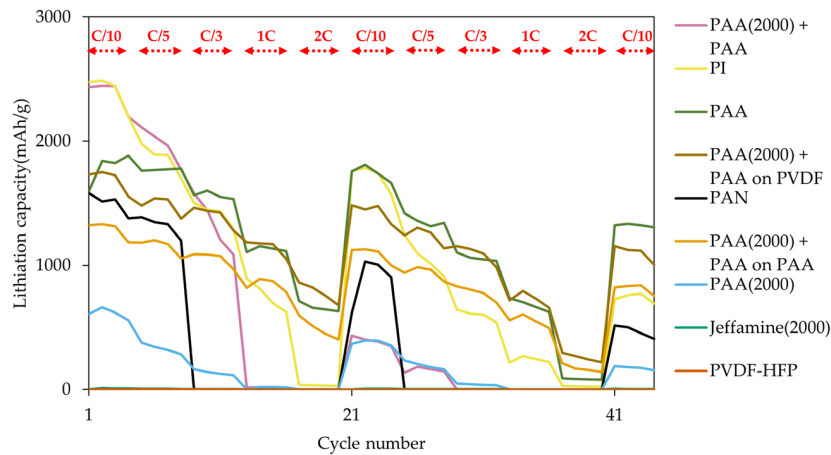


Figure 4.7: Capacity vs. cycle for Si electrodes made with different binder formulations. The C-rate is modified from one cycle to the next as indicated in the text.

4.3.2 Peeling test

Figure 4.8 presents the average peeling force vs. width of all the above-mentioned electrodes. In addition, we conducted the peeling test on two kinds of adhesion layer alone, namely PAA and PVDF adhesion layers. The peeling results indicate the mechanical integrity and adhesive strength of various binder materials to the copper current collector.

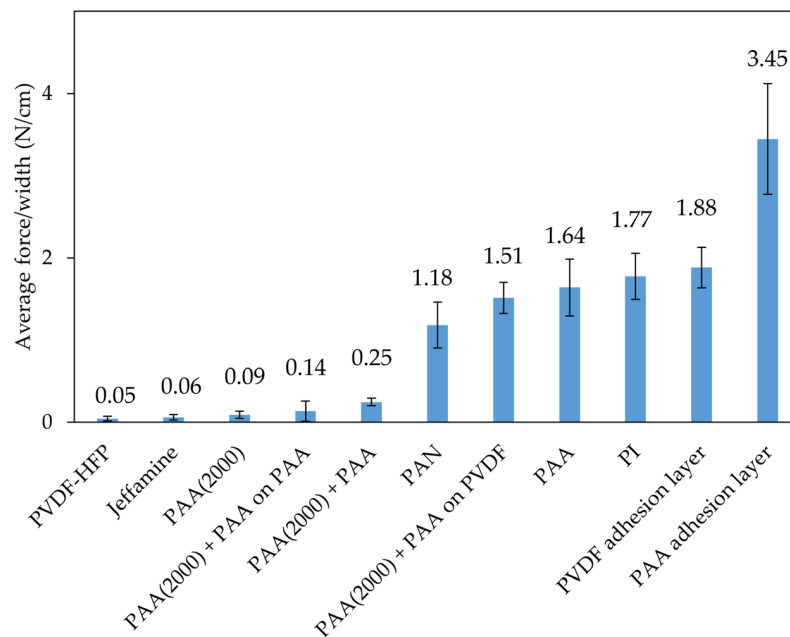


Figure 4.8: Average peeling force of electrode samples and two additional adhesion layer samples. Error bars indicate one standard deviation in the time-resolved sampling.

The peeling force measurements correlate well with the electrochemical performance shown in Figure 4.7, maintaining a similar pattern of PI exhibiting higher peeling force, followed by PAN, and comparatively lower values for the Jeffamine and PVDF-HFP binders. This trend supports the hypothesis that the inferior performance of certain cells could be attributed to the weak adhesion between the electrode coating layer and the copper current collector.

The peeling forces of PAA(2000) + PAA bulk layer with and without PAA/PVDF adhesion layer were also examined. PAA(2000) shows a minimum peeling among these all electrodes, confirming the deleterious effect of short-chain polymer on coating adhesion. Both PAA and PVDF adhesion layers show excellent peeling resistance. The PAA adhesion layer exhibits an average peeling force of 3.5 N/cm. However, when this adhesion layer was coated with PAA bulk layer, the adhesion dramatically drops close to that of PAA(2000). This confirms our hypothesis that if the bulk and adhesion layer use the same solvent to dissolve the kind of binder, these two layers will dissolve in each other and thus damage the adhesion coating.

This phenomenon is further overcome by PAA(2000) + PAA on PVDF, where dissimilar binders and solvents were used for adhesion and bulk electrode layers. PAA(2000) + PAA on PVDF shows an average peeling force of 1.5 N/cm, which is much higher than that of PAA(2000) + PAA on PAA at 0.08 N/cm. This further indicates the success in improving the adhesion.

4.4 Conclusions

In this chapter, we examined three more binder performance issues compared to Chapter 2 and 3. We first used commercial short-chain PAA and Jeffamine binders to investigate the chain-length effect. Both cycling and peeling results confirm that this shortened polymer chain leads to deteriorated performance.

We also evaluated the performance of several novel binders that showed potential in other battery systems. PI shows a satisfactory capacity throughout all C-rates. However, the tested PVDF-HFP and PAN do not work sufficiently well for our silicon anode system.

Reference

1. Kim, T., Song, W., Son, D.-Y., Ono, L.K. and Qi, Y., *Lithium-ion batteries: outlook on present, future, and hybridized technologies*. Journal of materials chemistry A, 2019. 7(7): p. 2942-2964.
2. Deng, L., Zheng, Y., Zheng, X., Or, T., Ma, Q., Qian, L., Deng, Y., Yu, A., Li, J. and Chen, Z., *Design criteria for silicon -based anode binders in half and full cells*. Advanced Energy Materials, 2022. 12(31): p. 2200850.
3. Goodenough, J.B. and Park, K.-S., *The Li-ion rechargeable battery: a perspective*. Journal of the American Chemical Society, 2013. 135(4): p. 1167-1176.
4. Karuppasamy, K., Vikraman, D., Choi, J.-H., Bose, R., Nicholson, A., Maiyalagan, T. and Kim, H.-S., *Hybrid lithium-ion capacitors based on novel 1-butyl-3-methylimidazolium bis (nonafluorobutanesulfonyl imide)(BMImBNFSI) ionic liquid electrolytes: A detailed investigation of electrochemical and cycling behaviors*. Journal of Materials Research and Technology, 2020. 9(3): p. 5216-5227.
5. Lee, B.-S., Yang, H.-S., Jung, H., Jeon, S.-Y., Jung, C., Kim, S.-W., Bae, J., Choong, C.-L., Im, J. and Chung, U.-I., *Novel multi-layered 1-D nanostructure exhibiting the theoretical capacity of silicon for a super-enhanced lithium-ion battery*. Nanoscale, 2014. 6(11): p. 5989-5998.
6. Zaghib, K., Nadeau, G. and Kinoshita, K., *Effect of graphite particle size on irreversible capacity loss*. Journal of the Electrochemical Society, 2000. 147(6): p. 2110.
7. Obrovac, M., Christensen, L., Le, D.B. and Dahn, J.R., *Alloy design for lithium-ion battery anodes*. Journal of The Electrochemical Society, 2007. 154(9): p. A849.
8. Louli, A., Li, J., Trussler, S., Fell, C.R. and Dahn, J., *Volume, pressure and thickness evolution of Li-ion pouch cells with silicon-composite negative electrodes*. Journal of The Electrochemical Society, 2017. 164(12): p. A2689.
9. Schweidler, S., De Biasi, L., Schiele, A., Hartmann, P., Brezesinski, T. and Janek, J.R., *Volume changes of graphite anodes revisited: a combined operando X-ray diffraction and in situ pressure analysis study*. The Journal of Physical Chemistry C, 2018. 122(16): p. 8829-8835.
10. Gu, M., Xiao, X.-C., Liu, G., Thevuthasan, S., Baer, D.R., Zhang, J.-G., Liu, J., Browning, N.D. and Wang, C.-M., *Mesoscale origin of the enhanced cycling-stability of the Si-conductive polymer anode for Li-ion batteries*. Scientific Reports, 2014. 4(1): p. 3684.

11. McDowell, M.T., Lee, S.W., Nix, W.D. and Cui, Y., *25th anniversary article: understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries*. *Advanced materials*, 2013. **25**(36): p. 4966-4985.
12. Shen, H., Wang, Q., Chen, Z., Rong, C. and Chao, D., *Application and development of silicon anode binders for lithium-ion batteries*. *Materials*, 2023. **16**(12): p. 4266.
13. Mei, J., Zhou, W., Ren, Y., Ding, P., Jiang, W. and Li, H. *Stress Evolution Prediction for Silicon Anode Particle during Charging/Discharging and a Comparison with In-Situ Test Results*. in *245th ECS Meeting (May 26-30, 2024)*. 2024. ECS.
14. Yu, D.Y., Zhao, M. and Hoster, H.E., *Suppressing vertical displacement of lithiated silicon particles in high volumetric capacity battery electrodes*. *ChemElectroChem*, 2015. **2**(8): p. 1090-1095.
15. Yu, Z., Cui, L., Zhong, B. and Qu, G., *Research progress on the structural design and optimization of silicon anodes for lithium-ion batteries: a mini-review*. *Coatings*, 2023. **13**(9): p. 1502.
16. Li, J.-Y., Xu, Q., Li, G., Yin, Y.-X., Wan, L.-J. and Guo, Y.-G., *Research progress regarding Si-based anode materials towards practical application in high energy density Li-ion batteries*. *Materials Chemistry Frontiers*, 2017. **1**(9): p. 1691-1708.
17. Wu, F., Dong, Y., Su, Y., Wei, C., Chen, T., Yan, W., Ma, S., Ma, L., Wang, B. and Chen, L., *Benchmarking the Effect of Particle Size on Silicon Anode Materials for Lithium-Ion Batteries*. *Small*, 2023. **19**(42): p. 2301301.
18. Kim, H., Seo, M., Park, M.H. and Cho, J., *A critical size of silicon nano-anodes for lithium rechargeable batteries*. *Angewandte Chemie International Edition*, 2010. **49**(12): p. 2146-2149.
19. Zhu, G., Wang, Y., Yang, S., Qu, Q. and Zheng, H., *Correlation between the physical parameters and the electrochemical performance of a silicon anode in lithium-ion batteries*. *Journal of Materiomics*, 2019. **5**(2): p. 164-175.
20. Kim, J.S., Pfleging, W., Kohler, R., Seifert, H.J., Kim, T.Y., Byun, D., Jung, H.-G., Choi, W. and Lee, J.K., *Three-dimensional silicon/carbon core-shell electrode as an anode material for lithium-ion batteries*. *Journal of Power Sources*, 2015. **279**: p. 13-20.
21. Chae, S., Choi, S.H., Kim, N., Sung, J. and Cho, J., *Integration of graphite and silicon anodes for the commercialization of high-energy lithium-ion batteries*. *Angewandte Chemie International Edition*, 2020. **59**(1): p. 110-135.
22. Rodrigues, M.-T.F., Rajendran, S., Trask, S.E., Dunlop, A.R., Singh, A., Allen, J.M., Weddle, P.J., Preimesberger, J.I., Coyle, J. and

- Colclasure, A.M., *Cell-format-dependent mechanical damage in silicon anodes*. ACS Applied Energy Materials, 2023. **6**(18): p. 9243-9248.
23. Müllner, S., Michlik, T., Reichel, M., Held, T., Moos, R. and Roth, C., *Effect of Water-Soluble CMC/SBR Binder Ratios on Si-rGO Composites Using μ m-and nm-Sized Silicon as Anode Materials for Lithium-Ion Batteries*. Batteries, 2023. **9**(5): p. 248.
 24. Lee, D., Park, H., Goliaszewski, A., Byeun, Y.-K., Song, T. and Paik, U., *In situ cross-linked carboxymethyl cellulose-polyethylene glycol binder for improving the long-term cycle life of silicon anodes in Li ion batteries*. Industrial & Engineering Chemistry Research, 2019. **58**(19): p. 8123-8130.
 25. Sun, F. and Wheeler, D.R., *The Effects of Lithium Ions and pH on the Function of Polyacrylic Acid Binder for Silicon Anodes*. Journal of The Electrochemical Society, 2023. **170**(8): p. 080502.
 26. Li, S., Liu, Y.-M., Zhang, Y.-C., Song, Y., Wang, G.-K., Liu, Y.-X., Wu, Z.-G., Zhong, B.-H., Zhong, Y.-J. and Guo, X.-D., *A review of rational design and investigation of binders applied in silicon-based anodes for lithium-ion batteries*. Journal of Power Sources, 2021. **485**: p. 229331.
 27. Li, P., Kim, H., Myung, S.-T. and Sun, Y.-K., *Diverting exploration of silicon anode into practical way: a review focused on silicon-graphite composite for lithium ion batteries*. Energy Storage Materials, 2021. **35**: p. 550-576.
 28. Zuo, X., Zhu, J., Müller-Buschbaum, P. and Cheng, Y.-J., *Silicon based lithium-ion battery anodes: A chronicle perspective review*. Nano Energy, 2017. **31**: p. 113-143.
 29. Franco Gonzalez, A., Yang, N.-H. and Liu, R.-S., *Silicon anode design for lithium-ion batteries: progress and perspectives*. The Journal of Physical Chemistry C, 2017. **121**(50): p. 27775-27787.
 30. Sun, L., Liu, Y., Shao, R., Wu, J., Jiang, R. and Jin, Z., *Recent progress and future perspective on practical silicon anode-based lithium ion batteries*. Energy Storage Materials, 2022. **46**: p. 482-502.
 31. Zhao, C., Wada, T., De Andrade, V., Gürsoy, D., Kato, H. and Chen-Wiegart, Y.-C.K., *Imaging of 3D morphological evolution of nanoporous silicon anode in lithium ion battery by X-ray nano-tomography*. Nano energy, 2018. **52**: p. 381-390.
 32. Mitchell, S.L. and Ortiz, M., *Computational multiobjective topology optimization of silicon anode structures for lithium-ion batteries*. Journal of power sources, 2016. **326**: p. 242-251.
 33. Huang, W., Wang, W., Wang, Y., Qu, Q., Jin, C. and Zheng, H., *Overcoming the fundamental challenge of PVDF binder use with silicon anodes with a super-molecular nano-layer*. Journal of Materials Chemistry A, 2021. **9**(3): p. 1541-1551.

34. Parikh, P., Sina, M., Banerjee, A., Wang, X., D'souza, M.S., Doux, J.-M., Wu, E.A., Trieu, O.Y., Gong, Y. and Zhou, Q., *Role of polyacrylic acid (PAA) binder on the solid electrolyte interphase in silicon anodes*. Chemistry of Materials, 2019. **31**(7): p. 2535-2544.
35. Wang, Y., Xu, H., Chen, X., Jin, H. and Wang, J., *Novel constructive self-healing binder for silicon anodes with high mass loading in lithium-ion batteries*. Energy Storage Materials, 2021. **38**: p. 121-129.
36. Ling, M., Zhao, H., Xiaoc, X., Shi, F., Wu, M., Qiu, J., Li, S., Song, X., Liu, G. and Zhang, S., *Low cost and environmentally benign crack-blocking structures for long life and high power Si electrodes in lithium ion batteries*. Journal of Materials Chemistry A, 2015. **3**(5): p. 2036-2042.
37. Hu, B., Jiang, S., Shkrob, I.A., Zhang, J., Trask, S.E., Polzin, B.J., Jansen, A., Chen, W., Liao, C. and Zhang, Z., *Understanding of pre-lithiation of poly (acrylic acid) binder: striking the balances between the cycling performance and slurry stability for silicon-graphite composite electrodes in Li-ion batteries*. Journal of Power Sources, 2019. **416**: p. 125-131.
38. Dang, D., Wang, Y., Wang, M., Hu, J., Ban, C. and Cheng, Y.-T., *Lithium Substituted Poly (acrylic acid) as a mechanically robust binder for low-cost silicon microparticle electrodes*. ACS Applied Energy Materials, 2020. **3**(11): p. 10940-10949.
39. Michaels, A. and Morelos, O., *Polyelectrolyte adsorption by kaolinite*. Industrial & Engineering Chemistry, 1955. **47**(9): p. 1801-1809.
40. Vogel, J.E., Sederholm, J.G., Shumway, E.M., Abello, G.J., Trask, S.E., Wheeler, D.R. and Mazzeo, B.A., *Li-ion battery electrode contact resistance estimation by mechanical peel test*. Journal of the Electrochemical Society, 2022. **169**(8): p. 080508.
41. Luduena, G.A., KuHne, T.D. and Sebastiani, D., *Mixed Grotthuss and vehicle transport mechanism in proton conducting polymers from ab initio molecular dynamics simulations*. Chemistry of Materials, 2011. **23**(6): p. 1424-1429.
42. Pieczonka, N.P., Borgel, V., Ziv, B., Leifer, N., Dargel, V., Aurbach, D., Kim, J.H., Liu, Z., Huang, X. and Krachkovskiy, S.A., *Lithium polyacrylate (LiPAA) as an advanced binder and a passivating agent for high-voltage Li-ion batteries*. Advanced Energy Materials, 2015. **5**(23): p. 1501008.
43. Shi, Z., Jiang, S., Robertson, L.A., Zhao, Y., Sarnello, E., Li, T., Chen, W., Zhang, Z. and Zhang, L., *Restorable neutralization of poly (acrylic acid) binders toward balanced processing properties and cycling performance for silicon anodes in lithium-ion batteries*. ACS Applied Materials & Interfaces, 2020. **12**(52): p. 57932-57940.

44. Hays, K.A., Armstrong, B. and Veith, G.M., *Ending the chase for a perfect binder: role of surface chemistry variation and its influence on silicon anodes*. ChemElectroChem, 2020. 7(18): p. 3790-3797.
45. Kwon, T., Jeong, Y.K., Lee, I., Kim, T.-S., Choi, J.W. and Coskun, A., *Systematic molecular-level design of binders incorporating Meldrum's acid for silicon anodes in lithium rechargeable batteries*. Advanced materials (Deerfield Beach, Fla.), 2014. 26(47): p. 7979-7985.
46. Xiong, J., Dupré, N., Mazouzi, D., Guyomard, D., Roué, L. and Lestriez, B., *Influence of the polyacrylic acid binder neutralization degree on the initial electrochemical behavior of a silicon/graphite electrode*. ACS Applied Materials & Interfaces, 2021. 13(24): p. 28304-28323.
47. Lee, S., Koo, H., Kang, H.S., Oh, K.-H. and Nam, K.W., *Advances in Polymer Binder Materials for Lithium-Ion Battery Electrodes and Separators*. Polymers, 2023. 15(23): p. 4477.
48. Yoo, M., Frank, C.W. and Mori, S., *Interaction of poly (vinylidene fluoride) with graphite particles. 1. Surface morphology of a composite film and its relation to processing parameters*. Chemistry of materials, 2003. 15(4): p. 850-861.
49. Yoo, M., Frank, C.W., Mori, S. and Yamaguchi, S., *Interaction of poly (vinylidene fluoride) with graphite particles. 2. Effect of solvent evaporation kinetics and chemical properties of PVDF on the surface morphology of a composite film and its relation to electrochemical performance*. Chemistry of materials, 2004. 16(10): p. 1945-1953.
50. Zhao, X., Niketic, S., Yim, C.-H., Zhou, J., Wang, J. and Abu-Lebdeh, Y., *Revealing the role of poly (vinylidene fluoride) binder in Si/graphite composite anode for Li-ion batteries*. ACS omega, 2018. 3(9): p. 11684-11690.
51. Burdette-Trofimov, M.K., Armstrong, B.L., Korkosz, R.J., Tyler, J.L., Mcauliffe, R.D., Heroux, L., Doucet, M., Hoelzer, D.T., Kanbargi, N. and Naskar, A.K., *Understanding the solution dynamics and binding of a PVDF binder with silicon, graphite, and NMC materials and the influence on cycling performance*. ACS Applied Materials & Interfaces, 2022. 14(20): p. 23322-23331.
52. Kasinathan, R., Marinaro, M., Axmann, P. and Wohlfahrt-Mehrens, M., *Influence of the molecular weight of poly -acrylic acid binder on performance of Si - alloy/graphite composite anodes for lithium - ion batteries*. Energy Technology, 2018. 6(11): p. 2256-2263.
53. Hu, B., Zhang, J., Zhang, S., Zhang, Z. and Zhang, L. *Molecular Weight Effect of Poly (Acrylic Acid) on the Silicon Anode of Lithium-Ion Batteries*. in *Electrochemical Society Meeting Abstracts* 231. 2017. The Electrochemical Society, Inc.
54. Hu, B., Shkrob, I.A., Zhang, S., Zhang, L., Zhang, J., Li, Y., Liao, C., Zhang, Z., Lu, W. and Zhang, L., *The existence of optimal molecular*

- weight for poly (acrylic acid) binders in silicon/graphite composite anode for lithium-ion batteries. *Journal of Power Sources*, 2018. **378**: p. 671-676.
55. Wang, M., Hu, J., Wang, Y. and Cheng, Y.-T., *The influence of polyvinylidene fluoride (PVDF) binder properties on LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂ (NMC) electrodes made by a dry-powder-coating process.* *Journal of The Electrochemical Society*, 2019. **166**(10): p. A2151.
 56. Wootthikanokkhan, J. and Changsuwan, P., *Dehydrofluorination of PVDF and proton conductivity of the modified PVDF/sulfonated SEBS blend membranes.* *J. Met. Mater. Miner*, 2008. **18**(2): p. 57-62.
 57. Marshall, J.E., Zhenova, A., Roberts, S., Petchey, T., Zhu, P., Dancer, C.E., Mcelroy, C.R., Kendrick, E. and Goodship, V., *On the solubility and stability of polyvinylidene fluoride.* *Polymers*, 2021. **13**(9): p. 1354.
 58. Kise, H. and Ogata, H., *Phase transfer catalysis in dehydrofluorination of poly (vinylidene fluoride) by aqueous sodium hydroxide solutions.* *Journal of Polymer Science: Polymer Chemistry Edition*, 1983. **21**(12): p. 3443-3451.
 59. Xiao, L., Davenport, D.M., Ormsbee, L. and Bhattacharyya, D., *Polymerization and functionalization of membrane pores for water related applications.* *Industrial & engineering chemistry research*, 2015. **54**(16): p. 4174-4182.
 60. Mecozzi, F., Dong, J.J., Angelone, D., Browne, W.R. and Eisink, N.N., *Oxidative cleavage of alkene C= C bonds using a manganese catalyzed oxidation with H₂O₂ combined with periodate oxidation.* *European Journal of Organic Chemistry*, 2019. **2019**(42): p. 7151-7158.
 61. Rajagopalan, A., Lara, M. and Kroutil, W., *Oxidative alkene cleavage by chemical and enzymatic methods.* *Advanced Synthesis & Catalysis*, 2013. **355**(17): p. 3321-3335.
 62. Lee, D.G. and Chen, T., *Cleavage reactions*, in *Comprehensive organic synthesis*. 1991, Pergamon Press Oxford. p. 541-591.
 63. Fisher, T.J. and Dussault, P.H., *Alkene ozonolysis.* *Tetrahedron*, 2017. **73**(30): p. 4233-4258.
 64. Tkachenko, Y. and Niedzielski, P., *FTIR as a method for qualitative assessment of solid samples in geochemical research: A review.* *Molecules*, 2022. **27**(24): p. 8846.
 65. Zimudzi, T.J., Feldman, K.E., Sturnfield, J.F., Roy, A., Hickner, M.A. and Stafford, C.M., *Quantifying carboxylic acid concentration in model polyamide desalination membranes via Fourier transform infrared spectroscopy.* *Macromolecules*, 2018. **51**(17): p. 6623-6629.
 66. Wang, Y., Wang, H., Liu, K., Wang, T., Yuan, C. and Yang, H., *Effect of dehydrofluorination reaction on structure and properties of PVDF electrospun fibers.* *RSC advances*, 2021. **11**(49): p. 30734-30743.

67. Kise, H., Ogata, H. and Nakata, M., *Chemical dehydrofluorination and electrical conductivity of poly (vinylidene fluoride) films*. Die Angewandte Makromolekulare Chemie: Applied Macromolecular Chemistry and Physics, 1989. **168**(1): p. 205-216.
68. Dias, A.J. and McCarthy, T.J., *Dehydrofluorination of poly (vinylidene fluoride) in dimethylformamide solution: Synthesis of an operationally soluble semiconducting polymer*. Journal of Polymer Science: Polymer Chemistry Edition, 1985. **23**(4): p. 1057-1061.
69. Schwaderer, J., Drache, M. and Beuermann, S., *Temperature Dependence of the Number of Defect-Structures in Poly (vinylidene fluoride)*. Molecules, 2024. **29**(7): p. 1551.
70. Yao, D., Feng, J., Wang, J., Deng, Y. and Wang, C., *Synthesis of silicon anode binders with ultra-high content of catechol groups and the effect of molecular weight on battery performance*. Journal of Power Sources, 2020. **463**: p. 228188.
71. Porcher, W., Chazelle, S., Boulineau, A., Mariage, N., Alper, J., Van Rompaey, T., Bridel, J.-S. and Haon, C., *Understanding polyacrylic acid and lithium polyacrylate binder behavior in silicon based electrodes for Li-ion batteries*. Journal of The Electrochemical Society, 2017. **164**(14): p. A3633.
72. Aldalur, I., Armand, M. and Zhang, H., *Jeffamine-based polymers for rechargeable batteries*. Batteries & Supercaps, 2020. **3**(1): p. 30-46.
73. Aldalur, I., Zhang, H., Piszcz, M., Oteo, U., Rodriguez-Martinez, L.M., Shanmukaraj, D., Rojo, T. and Armand, M., *Jeffamine® based polymers as highly conductive polymer electrolytes and cathode binder materials for battery application*. Journal of Power Sources, 2017. **347**: p. 37-46.
74. Le, A.V., Wang, M., Noelle, D.J., Shi, Y., Shirley Meng, Y., Wu, D., Fan, J. and Qiao, Y., *Using high -HFP -content cathode binder for mitigation of heat generation of lithium -ion battery*. International Journal of Energy Research, 2017. **41**(14): p. 2430-2438.
75. Shi, X.-D., Liu, Z.-X., Zhou, Y.-F., Wang, P.-J., Jiang, Z. and Liang, S.-Q., *PVDF- HFP binder for advanced zinc- manganese batteries*. Transactions of Nonferrous Metals Society of China, 2022. **32**(9): p. 3005-3014.
76. Luo, L., Xu, Y., Zhang, H., Han, X., Dong, H., Xu, X., Chen, C., Zhang, Y. and Lin, J., *Comprehensive understanding of high polar polyacrylonitrile as an effective binder for Li-ion battery nano-Si anodes*. ACS applied materials & interfaces, 2016. **8**(12): p. 8154-8161.
77. Gong, L., Nguyen, M.H.T. and Oh, E.-S., *High polar polyacrylonitrile as a potential binder for negative electrodes in lithium ion batteries*. Electrochemistry communications, 2013. **29**: p. 45-47.

78. Qian, G., Wang, L., Shang, Y., He, X., Tang, S., Liu, M., Li, T., Zhang, G. and Wang, J., *Polyimide binder: a facile way to improve safety of lithium ion batteries*. *Electrochimica Acta*, 2016. **187**: p. 113-118.
79. Kim, J.S., Choi, W., Cho, K.Y., Byun, D., Lim, J. and Lee, J.K., *Effect of polyimide binder on electrochemical characteristics of surface-modified silicon anode for lithium ion batteries*. *Journal of Power Sources*, 2013. **244**: p. 521-526.
80. Oh, J., Jin, D., Kim, K., Song, D., Lee, Y.M. and Ryou, M.-H., *Improving the cycling performance of lithium-ion battery Si/graphite anodes using a soluble polyimide binder*. *Acs Omega*, 2017. **2**(11): p. 8438-8444.
81. So, Y., Bae, H.-S., Kang, Y.Y., Chung, J.Y., Park, N.K., Kim, J., Jung, H.-T., Won, J.C., Ryou, M.-H. and Kim, Y.H., *Eco-friendly water-processable polyimide binders with high adhesion to silicon anodes for lithium-ion batteries*. *Nanomaterials*, 2021. **11**(12): p. 3164.