Joule

CellPress

Preview

Stretched to the Limit for Better Batteries

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Conventional polymeric binders used within Li-ion battery electrodes cannot withstand the large volume changes exhibited by high-capacity alloying anode materials such as silicon, resulting in fast capacity decay with cycling. In this issue of *Joule*, Xu and coworkers report a new cross-linked polymer binder that enables excellent capacity retention over hundreds of cycles in silicon microparticle-based electrodes. To achieve this performance, this binder strongly adheres to the silicon while also exhibiting substantial mechanical elasticity and self-healing functionality.

Alloying anode materials such as silicon hold great promise for improving the specific energy of Li-ion batteries.[1] These materials can hold substantially more lithium than conventional graphitic anodes, but this higher capacity comes at the price of much larger volumetric and structural changes during lithium insertion and removal.[2] These changes cause degradation of the electrochemical performance of silicon anodes during cycling through a variety of pathways. Particles with sizes above a few hundred nanometers can fracture, resulting in loss of electrical contact and capacity decay if the fractured pieces are not held in place. Volumetric changes during reactions also continually expose new surface area to the electrolyte, which accelerates solid-electrolyte-interphase (SEI) formation and leads to low Coulombic efficiency. Together, these phenomena often result in a rapid loss of capacity with cycling of silicon anodes.

A significant amount of research has been performed with the goal of engineering nanoscale silicon materials to avoid fracture and to dimensionally stabilize the interface with the electrolyte.[3] While interesting nanostructures have been developed that have yielded good cycle life, such as yolk-shell particles,[4] there are significant challenges with implementing nanostructure-based electrodes in real batteries. This is partly because nanostructures unavoidably have higher surface area than micron-scale particles, which increases the prevalence of side reactions. Nanostructures are also more difficult to pack efficiently into an electrode, which reduces volumetric energy density. Finally, nanostructured silicon is generally expensive to make, especially when considering the scale necessary for battery manufacturing.

Rather than carefully engineering the size, shape, and structure of the active silicon particles, another strategy has been to instead develop new polymeric binders designed to more effectively hold silicon particles together during electrochemical cycling.[5–8] All battery electrodes contain small amounts of polymeric binder and conductive carbon additives, which function to maintain the mechanical integrity of the electrode architecture and to improve electrical conductivity, respectively. To be effective for silicon electrodes, a binder must exhibit good mechanical elasticity, and it also should chemically bind to and passivate the surface of the silicon. Polyvinylidene fluoride (PVDF) is the binder that is commonly used in electrodes with conventional, small-volume-change active battery materials, but PVDF exhibits poor performance with silicon electrodes.[9] Recent work has shown that poly(acrylic acid)-based binders are particularly effective at improving capacity retention with cycling.[9] It is thought that poly(acrylic acid) (PAA) can both bind to and passivate the surface of silicon, which decreases side reactions with the electrolyte. However, PAA itself is not elastic enough to withstand the extreme volume changes of silicon. Recently, PAA cross-linked with polyrotaxane molecules was shown to exhibit excellent capacity retention during cycling within silicon microparticle anodes.[7] Polyrotaxanes undergo a ring-sliding mechanism during deformation, which allows this reported binder to undergo ∼200% reversible strains, thus effectively holding together the silicon particles. While the synthetic procedures to fabricate these binders are complex, this work illustrates the promise of cross-linking for the design of binders with multiple functionalities.

In this month's issue of *Joule*, Xu et al. report a new cross-linked binder that shows superb cycling performance for silicon microparticle anodes.[10] This binder is made up of PAA cross-linked with poly(2-hydroxyethyl acrylate-codopamine methacrylate), or p(HEA-co-DMA). This material shows interesting properties that likely enable the stable cycling of silicon anodes. In contrast to pure PAA, the cross-linked network shows the ability to reversibly undergo large strains, with 150% reversible strain demonstrated in mechanical tests. The binder material also shows evidence of "self-healing,"

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meaning that chemical bonds are formed when two separated pieces of the polymer are brought together. This is thought to be important for binders for large-volume-change battery materials, as self-healing can mitigate mechanical damage in local areas undergoing extreme morphological changes (such as near a crack). Importantly, both types of polymer chains act synergistically to enable promising performance: the PAA chains adhere to the silicon and provide mechanical strength, while the p(HEA-co-DMA) chains provide elasticity and self-healing ability. The authors hypothesize that these features enable the silicon particles within the electrode to be more effectively held together with less extensive surface side reactions during expansion and contraction of the electrode (Figure 1).

This binder is shown to enable excellent electrochemical cycling for silicon microparticle-based electrodes. The electrodes show stable cycling over hundreds of cycles, as compared to steady capacity decay over the first 100 cycles for pure PAA binder. The authors also present good cyclability with areal specific capacities > 3 mAh cm^{-2}, which approaches that which is necessary for commercial cells. Post-mortem scanning electron microscopy (SEM) shows that the PAA-p(HEA-co-DMA) maintains an intact electrode structure after 100 cycles, whereas the use of pure PAA binder results in large cracks within the electrode. This supports the hypothesized mechanism of action of the binder. Finally, two aspects of the binder may allow electrodes to be manufactured at relatively low cost: the binder can be processed in aqueous solvents instead of traditional organic solvents, and it also can be used with silicon microparticles instead of engineered nanoparticles. The silicon microparticles used in the report are fabricated with ball-milling procedures, which ensures scalability.

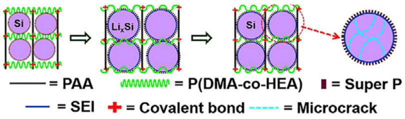

Figure 1. Schematic Showing Silicon Particles Surrounded by the Crosslinked PAA-p(HEA-co-DMA) Binder Network

Upon expansion and contraction of the silicon, the network stretches and maintains contact between particles even when internal microcracks form.

The combination of excellent cycling performance and the potential for low-cost production represent an important advance in the field of binders for large-volume-change anodes. Interestingly, the binder was reported to work very well for silicon particles under 3 μm in size, whereas particles with a size distribution between 2 and 6 μm were reported to perform poorly. Since larger particles can potentially be packed more effectively, this invites future research into designing binders that can improve the cycling performance of even larger particles.

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1. Obrovac, M.N., and Chevrier, V.L. (2014). Alloy negative electrodes for Li-ion batteries. Chem. Rev. *114*, 11444–11502.
2. McDowell, M.T., Lee, S.W., Nix, W.D., and Cui, Y. (2013). 25th anniversary article: Understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries. Adv. Mater. *25*, 4966–4985.
3. Chae, S., Ko, M., Kim, K., Ahn, K., and Cho, J. (2017). Confronting issues of the practical implementation of Si anode in high-energy lithium-ion batteries. Joule *1*, 47–60.
4. Liu, N., Lu, Z., Zhao, J., McDowell, M.T., Lee, H.-W., Zhao, W., and Cui, Y. (2014). A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. Nat. Nanotechnol. *9*, 187–192.
5. Magasinski, A., Zdyrko, B., Kovalenko, I., Hertzberg, B., Burtovyy, R., Huebner, C.F., Fuller, T.F., Luzinov, I., and Yushin, G. (2010). Toward efficient binders for Li-ion battery Si-based anodes: polyacrylic acid. ACS Appl. Mater. Interfaces *2*, 3004–3010.
6. Koo, B., Kim, H., Cho, Y., Lee, K.T., Choi, N.S., and Cho, J. (2012). A highly cross-linked polymeric binder for high-performance silicon negative electrodes in lithium ion batteries. Angew. Chem. Int. Ed. *51*, 8762–8767.
7. Choi, S., Kwon, T.-W., Coskun, A., and Choi, J.W. (2017). Highly elastic binders integrating polyrotaxanes for silicon microparticle anodes in lithium ion batteries. Science *357*, 279–283.
8. Wang, C., Wu, H., Chen, Z., McDowell, M.T., Cui, Y., and Bao, Z. (2013). Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries. Nat. Chem. *5*, 1042–1048.
9. Nguyen, C.C., Yoon, T., Seo, D.M., Guduru, P., and Lucht, B.L. (2016). Systematic investigation of binders for silicon anodes: Interactions of binder with silicon particles and electrolytes and effects of binders on solid electrolyte interphase formation. ACS Appl. Mater. Interfaces *8*, 12211–12220.
10. Xu, Z., Yang, J., Zhang, T., Nuli, Y., Wang, J., and Hirano, S.-I. (2018). Silicon microparticle anodes with self-healing multiple network binder. Joule *2*, this issue, 950–961.