

LITHIUM-ION BATTERIES

Stress relief for silicon



Our strategy combines the best of the covalent and non-covalent binder approaches



Silicon has gained much attention as an anode material in the research field of lithium-ion batteries. However, its high specific capacity is overshadowed by an insufficient number of charge–discharge cycles to achieve long-term applications. This limited cyclability arises from detrimental processes that occur because of huge volume changes experienced by silicon anodes during repeated lithiation and delithiation steps. This is a particular challenge for anodes

made from microparticles of silicon because of the pulverization of the microparticles and the ensuing side reactions with liquid electrolytes.

Now, writing in *Science*, Ali Coskun, Jang Wook Choi and colleagues reveal how an elastic binder material within silicon microparticle anodes can reduce the detrimental effect of these volume changes. The dual-component binder material uses a series of ‘molecular pulleys’ to dissipate the stress caused by the expansion and contraction of the anode. This stress-release mechanism lessens the disintegration of the microparticles, retains the morphology of the anode by maintaining the coalescence of the microparticles, and limits the growth of solid electrolyte interphase layers around the pulverized microparticles. In short, it reduces the negative effects usually introduced by the changes in volume of silicon anodes.

The binder material comprises a polyrotaxane that is covalently linked to a known binder polymer, polyacrylic acid (PAA). First, the polyrotaxane is made by threading polyethylene glycol (PEG) through α -cyclodextrin rings, and then molecular stoppers are added to both ends of the PEG chain. Second, some of the α -cyclodextrin rings of the polyrotaxane are crosslinked, by means of ester bonds, with the PAA chains. “The incorporation of only 5 wt% polyrotaxane to PAA completely transforms the mechanical properties,” says Coskun. “As a result of the ring-sliding motion of the rotaxanes, the binder material becomes highly stretchable and elastic and can tolerate up to 400% strain.”

In half-cell experiments using lithium metal as the counter electrode, the polyrotaxane–PAA silicon microparticle electrode shows less disintegration of the microparticles and better cyclability than the PAA–silicon microparticle electrode. “At a commercial level of areal capacity (about 3 mAh cm^{−2}), silicon microparticle anodes operate for no more than tens of charge–discharge cycles, but on integration of the stretchable binder, the number of charge–discharge cycles extends to more than 500 cycles,” says Choi.

On lithiation, the polyrotaxane–PAA chains stretch and the cyclodextrin rings that are otherwise randomly placed along the thread come closer to each other to reduce the mechanical stress. On delithiation, the rings go back to their random positions as a consequence of entropic repulsion. “Our strategy combines the best of the covalent and non-covalent binder approaches in the form of a mechanical bond embodied in the polyrotaxane,” explains Coskun.

The commercialization of the binder material in a conventional battery production line is the future goal of the researchers. “In particular, we are trying to lower the binder content of the anode (10 wt% in the current method), and from a manufacturing perspective, we are testing various parameters in battery processing, such as the viscosity of the electrode slurry,” concludes Choi.

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