

# Polyrotaxane Molecular Pulleys: Highly Elastic Binder for Silicon Microparticle Anodes in Lithium Ion Batteries

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The recent advent of electric vehicles is demanding lithium-ion batteries (LIBs) with higher energy densities. Although Silicon (Si) anodes have an exceptional theoretical capacity of over 3000 mAh g<sup>-1</sup>, they suffer from notorious volume expansion upon cycling (up to 300 %), leading to short charge-discharge cycle life. The volume expansion causes the pulverization of Si particles, the delamination of the electrode film, and the formation of an unstable SEI layer. It has been revealed that polymeric binder can play a critical role in mitigating these failure modes. However, their effect is usually proven mainly for nanometer-scale Si particles. Unfortunately, when it comes to micron-sized Si particle (SiMP) under commercial operation conditions, binder functions are largely weakened.

Polyrotaxane (PR) consists of polyethylene glycol (PEG) threads interlocked with  $\alpha$ -cyclodextrin ( $\alpha$ -CD) rings. When  $\alpha$ -CD rings in PR are covalently crosslinked with polyacrylic acid (PAA), named as PR-PAA, these rings can “slide” along the PEG thread. Due to the sliding motion of the  $\alpha$ -CD rings, the PRs are key to lowering the stress exerted on the PR-PAA. Thus, the binder film endured up to 390% strain. In the given polymeric network, the ring-sliding of PRs can reduce the mechanical stress generated during the volume expansion of Si active materials. The stress dissipation mechanism is analogous to the operation of moving pulleys [1].

In electrochemical tests with a half-cell, the SiMP electrode based on the PR-PAA binder (PR-PAA-SiMP) with an areal capacity of 3.18 mAh cm<sup>-2</sup>, shows robust cycling performance with 91% capacity retention after 150 cycles at 0.2C (0.64 mA cm<sup>-2</sup>). In addition, a full-cell pairing with LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) cathode showed a 98% capacity retention after 50 cycles with a commercial level of areal capacity (2.88 mAh cm<sup>-2</sup>). Furthermore, in order to prove the crucial role of PR-PAA binder in SiMP electrodes, cross-sectional images of the electrodes were monitored with scanning electron microscopy (SEM). Whereas the use of a PAA binder resulted in pulverized SiMPs with thick SEI layer grown, the PR-PAA binder allows pulverized Si particles to remain coalesced thanks to the high elasticity of the binder, resulting in thin and stable SEI layers in inter-particle spaces. Thus, this study reveals the importance of high elasticity of a binder network in maintaining the high capacity battery operation that undergoes the large volume expansion.

## Reference:

[1] S. Choi, T. -w. Kwon, A. Coskun, J. W. Choi, *Science* 357 (2017) 279–283.