

A Commercial PAA/PVB-based Polymer Binder for Silicon Nanoparticle-Based Lithium-Ion Battery Anodes

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The use of Si as anode material in Li-ion batteries has attracted considerable attention over the last years, since Si is abundant, possesses a low charge-discharge potential of ~ 0.4 V vs Li/Li⁺ and a high theoretical gravimetric capacity (3579 mAhg^{-1} based on Li₁₅Si₄), which is an order of magnitude higher than the capacity of graphite anodes commercially available nowadays in Li-ion batteries.^{1,2} However, silicon anode materials exhibit a substantial volume change ($\sim 300\%$) during lithiation/delithiation, which causes significant challenges in preserving the electrode integrity and capacity retention during its operation. The formation of a thick solid electrolyte interphase (SEI) layer due to mechanical strains and poor electrical contact of Si particles to the conducting matrix requires the optimization of binder materials, which are pivotal for the realization of high capacity Si-based electrodes.

Our approach towards novel polymer binders includes the preparation and characterization of Si-electrodes with poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB). The molecular structure of PVB suggests a good adhesion to Cu, the oxide layer of Si-nanoparticles (Si-NPs) as well as conductive carbon additives, and *co*-polymerization with poly(acrylic acid) (PAA) offers various ratios between polymer chains and functional COOH and OH groups. The electrode performance has been correlated with the mechanical properties of composite polymer, measured by AFM tip indentation, and it was found that stiffness of a polymer binder is not a prerequisite for capacity retention. A strong influence of fluoroethylene carbonate (FEC) as electrolyte additive on the performance of an electrode containing only PVB as binder polymer suggests that PVB integrates into the SEI formation and eventually leads to its stabilization, as indicated by a prolonged cycle life.

We prepared electrodes containing 60 wt% Si-NPs (30-50 nm), 20 wt% carbon black and 20 wt% binder by the slurry coating method and tested them in Swagelok-cells with lithium metal discs as counter electrode cycling the cells between 0.01 and 1.2 V vs Li/Li⁺. Even at the relatively high areal loading of 1.5 mg/cm^2 , our system demonstrates a first cycle lithiation capacity of $2750 \text{ mAh/g}_{\text{el}}$ (based on the total electrode mass) and a first cycle efficiency of $\sim 82\%$. After 100 repeated cycles this electrode was still able to store $1400 \text{ mAh/g}_{\text{el}}$.

We also evaluated the interaction between PAA-PVB and a mixture of carbonates EC:DMC (1:1 v/v) by measuring the swellability of the polymer films by AFM. In an attempt to quantitatively examine the binder-Si interactions in single-molecular resolution, AFM pulling tests were conducted. To verify the formation of covalent bonding both within the PAA-PVB binder and between polymeric component and Si-NPs FTIR was conducted. SEM was applied to study morphology of the electrodes.

References:

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- [2] Li, J.; Dahn, J. R. *J. Electrochem. Soc.* 154 (2007) A156