

Brown algae-mimetic alginate binder with improved desolvation and resilience for use in Si-based anode binder of a lithium ion battery

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서론

The need for rechargeable lithium ion batteries (LIBs) has rapidly increased because of the growing smart phone and electric/hybrid vehicle markets. However, graphitic carbon-based anode, commonly used anode in LIBs, has suffered a low theoretical capacity problem (372 mA h g⁻¹). Thus, Si-based anodes in lithium ion batteries (LIBs) has been suggested as an alternative due to exceptionally high theoretical capacity (4200 mA h g⁻¹), low cost, and natural abundance.

However, the mechanical instability of Si-based anodes in LIBs has been the major barrier to their practical application. Generally, the Si-based anode is a composite composed of Si particles (active material), carbon (conducting agent), and polymeric binder. During the charging/discharging process, Li ion and Si undergo alloy-de-alloy phase transition to Li_{4.4}Si. As a consequence, the volume of Si particles expands over three-fold, which results in cracks and fractures of the anode composites due to the mechanical stress arising from the volume expansion. After all, it leads to a serious degradation of electrical contact between active materials and current collector. Thus, this problem shortens the battery cycling life time and is one of the main obstacles in commercialization of Si-based anodes in LIBs.

To overcome the mechanical damages of the anode composite, many researches have focused on developing polymeric binder for the anode composite. The physical and chemical properties of the binder have a critical effect on these abilities. The requirements of the binder are (i) to improve the adhesion strength between anode composite and current collector, (ii) to retain the binding with Si during Li-charging/discharging cycling, (iii) to decrease the Li ion loss by forming stable solid electrolyte interphase (SEI) layer. To date, biopolymers such as carboxymethyl cellulose (CMC) and alginate demonstrate promising performances as binders owing to their improved mechanical properties compared to commercially available Polyvinylidene fluoride (PVDF) binder. Some recent studies have revealed that the improved resilience of self-healable binders has contributed to the battery cyclic life time. The self-healing property of the binder can continuously repairs the mechanical damages in the binders during the sequential charging/discharging process; thereby it extend the Si-anode composite life in LIBs.

A bio-inspired chemistry of brown algae suggests insight to provide self-healing properties to the binders. Alginate, a bio-copolymer of β-D-mannuronate units (M block) and α-L-guluronate (G block) connected by 1,4 linkages, forms reversible and self-healable bond in

the presence of calcium (Ca) or magnesium (Mg) ions. in the cell walls of brown algae. Interestingly, alginate acquires extreme toughness and resilience in the presence of calcium ions. G blocks of alginate selectively couples with calcium ions. Thereby it forms a row of reversible and strong electrostatic cross-links called “the egg-box structure”. The high unzipping energy of the cross-links can enhance modulus, toughness, and re-zipping of the cross-links spontaneously heals the mechanical damages on the cell wall of brown algae.

In this study, we fabricated brown algae-mimetic Ca-alginate (calcium-doped alginate) binder for Si anode composite with enhanced stiffness, toughness, and resilience compared to Na-alginate (sodium alginate), CMC, and PVDF binders due to reversible Ca mediated cross-link. As a consequence, the Ca-alginate binder demonstrated better battery performance in terms of longer life time and higher charge capacity than the Na-alginate, CMC, and PVDF.

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본론

Improvement in electrolyte-desolvation and resilience of alginate

Electrolyte solvation of polymeric binders reduces molecular interaction strengths between binders or between binder and Si particles. Thus, electrolyte over-uptake of the binder can eventually deteriorate the battery performance due to softening of the binder and weak adhesion between the binder and the Si particle. Thus, we measured the electrolyte adsorption values of the binder films. Electrolyte absorption values of the alginate films regardless of calcium addition were much lower than PVDF (~165 %). Ca-alginate showed lower electrolyte uptake (~4.2 %) than Na-alginate (~8.7 %).²⁴ After EDTA treatment, the electrolyte-uptake of the Ca-alginate rose to ~9.0 %, which is comparable to Na-alginate. Presumably, the G-unit segments selectively surrounded Ca-ions preferable to solvation by electrolyte-molecule and then the egg-box cross-links prevented electrolyte-infiltration. The electrolyte absorption value of PVDF (~165 %) was much higher than those of the other biopolymer binders and the value of CMC (~8.8 %) was as low as that of Na-alginate. The results are likely due to the fact that PVDF is organo-soluble polymer while Na-alginate and CMC are water-soluble polymers.

To guarantee longer life time of binder against continuous mechanical stress during Li-charging/discharging process, mechanical properties of binder polymers fully solvated by electrolyte should be improved. The lower electrolyte (solvent) uptake of the Ca-alginate films than the control groups was expected to suppress solvation-driven softening of Ca-alginate, and the reversible and strong Ca-mediated cross-links were expected to improve stiffness, toughness, and resilience of the electrolyte-absorbed alginate. Therefore, tensile properties of electrolyte-absorbed Na-alginate were compared to those of electrolyte-absorbed Ca-alginate. The stiffness and toughness of the Ca-alginate in the presence of the electrolyte were 510 ± 21 MPa and 13.5 ± 3.1 MJ·m⁻³, respectively, and these values are much better than those of Na-alginate: 121 ± 6 MPa of stiffness and 4.8 ± 0.5 MJ/m³ of toughness. After EDTA treatment, the tensile properties of the electrolyte-absorbed Ca-alginate fell to level of the Na-alginate: 132 ± 12 MPa of stiffness and 3.3 ± 0.6 MJ·m⁻³ of toughness. The results suggest that the addition of Ca ions to alginate film caused better tensile properties of the Ca-alginate than the Na-alginate film. Tensile properties of the electrolyte-absorbed Ca-alginate were superior to those of commercial binders such as PVDF (32 ± 2 MPa of stiffness, 1.2 ± 0.1 MJ·m⁻³ of

toughness) and CMC (112 ± 19 MPa of stiffness, 2.8 ± 0.1 MJ•m⁻³ of toughness). Probably, the improved tensile properties of Ca-alginate compared to the others is attributed to high un-zipping energy of the egg-box structure.

The resilience of a binder, the ability of a binder to re-cover original state after cyclic mechanical stress, is also an important mechanical parameter. Strain recovery of electrolytes-solvated Na-alginate, Ca-alginate, and EDTA-treated Ca-alginate were monitored during cyclic tensile tests with different loading strain (5, 10, and 20 %) (Figure 3b, 3c, 3d, 3e). At 5% of loading strain, Ca-alginate film exhibited gradual decrease of the strain recovery value to ~65 % at 20th cycle but was not broken even after 20 times cycles. However, Na-alginate film at the same condition exhibited the dramatic decrease of the strain recovery value and was readily broken only at less than 3 times cycles. At both 10 % and 20 % of loading strain tests, the Ca-alginate exhibited relatively slower the decrease of the strain recovery value than Na-alginate while Na-alginate exhibited the dramatic decrease and the break at less than 2 cycles. To further understand the effect of Ca ions into resilience of alginate, the same tensile tests was performed on the EDTA treated Ca-alginate film. After the EDTA treatment, the resilience of the Ca-doped alginate fell again to level of the Na-alginate. These results support that the Ca-alginate complex improved the resilience of alginate by spontaneously healing the internal damage via re-zipping of the egg-box structure.

Electrochemical Performance

Based on experimental results and discussion above, the electrostatic cross-links of the Ca-alginate binder contributing to the high capacity and stable cycling life time of battery performance can be proposed as follows: First, Ca-alginate binder has low value of the electrolyte-uptake and it means there is weak interaction between binder and electrolyte. Generally, if binder uptakes excessive electrolyte, it may not provide sufficient binding with Si particles and lead to relatively rapid degradation of Si.³¹ Therefore, the lowest electrolyte uptake of the Ca-alginate binder among the tested binders prevents Si particles from decomposing during the cycling test by retaining adhesion of binder to Si particles in the anode.

Second, the unique molecular structure and the chemistry of alginate may account for the excellent performance as LIB. Alginate is copolymer consisting of M block and G block monomers with carboxylic acid functional groups. Carboxyl groups of alginate may form hydrogen bonding with the oxide layer of Si surface and a row of G blocks in alginate has regular helical structure that enhance interactions between binders.¹⁶ Though CMC also has carboxylic acid groups, its molecular conformation is random coil.³² We demonstrated that the electrostatic bonds between Ca and alginate provide high toughness and resilience arising from spontaneously repeating zipping and unzipping of Ca-mediated egg-box structure. Consequently, enhanced extensibility, toughness, and resilience of Ca-alginate may assist to hold cracked Si particles, thereby withstanding Si degradation from large volume change during cycling. To provide further confirmation of the effect of Ca-alginate binder, the thickness of each Si electrode was examined by ex-situ scanning electron microscopy (SEM).⁸ We disassembled the each Si electrode after 300 cycles. The Si-CA electrode had increased thickness by 2.7 times, whereas that of Si-A electrode was 4.3 times. From SEM images, it is derived that this electrostatic crosslink of Ca-alginate is able to accommodate volume change of Si and retain cracked Si effectively.

Third, we inferred Ca-alginate binder allow the formation of a relatively stable and deformable solid electrolyte interphase (SEI). The high Coulombic efficiency (CE) indicates reversibility of electrode and stable SEI formation. Earlier research on alginate binder suggested that the alginate binder contributes to building a stable SEI layer on the Si surface. Add to this, we achieved more improvements in SEI layer by making electrostatic cross links between Ca and Alginate. As shown in Figure 5 b, the average CE values are higher in Si-CA electrode than those of Si-A electrode. The Si-A electrode suffered from repeating significant volume change, which makes Si particle break, thereby appearing pure Si in broken parts and form additional SEI layer in there. On the contrary, the high CE value in Si-CA electrode suggests that the Ca-alginate binder minimized Li ion loss on the electrode surface and prevented collapse of Si electrode by retaining anode composite during the cycles.

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결론

Ca-alginate binder demonstrated promising mechanical properties that endure catastrophic volume change of silicon-anode owing to Ca-mediated “egg-box” like electrostatic cross-links. High unzipping energy, spontaneous re-zipping, and electrolyte-desolvation of the cross-links provided significant improvement in stiffness, toughness, and resilience of the electrolyte-solvated alginate binder compared to Na-alginate and other commercial binders. Consequently, the improved mechanical properties of Ca-doped alginate are directly translated into enhancing lifetime and capacity of Si-based-anode LIB. This strategy expands the possibility of the alginate as silicon anode binder of LIB.