Self-healing chemistry based on hydrogen bonding between a hydroxyl-rich binder and an oxygen-rich active material was developed for stable Na-ion batteries. The strong chemical bonding between the binder and active material self-heals the cracks of active material upon cycling, resulting in outstanding cycling stability. This self-healing strategy is promising for developing high-energy and high-stability rechargeable batteries.

Chao Luo, Xiulin Fan, Zhaohui Ma, Tao Gao, Chunsheng Wang
cswang@umd.edu

HIGHLIGHTS
Development of self-healing chemistry between organic material and binder
Hydrogen bonding between organic material and binder self-heals cracks upon cycling
The self-healing electrode exhibits a stable cycle life in Na-ion batteries

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Self-Healing Chemistry between Organic Material and Binder for Stable Sodium-Ion Batteries

Chao Luo, Xiulin Fan, Zhaohui Ma, Tao Gao, and Chunsheng Wang

SUMMARY
One of the major challenges for high-energy sodium-ion batteries is the mechanical fracture triggered by large volume change. To circumvent pulverization-induced capacity decay, self-healing chemistry between binder and active material is critical but is never reported. Here, we report a self-healing electrode with hydrogen bonding between an oxygen-rich active material, sodium rhodizionate dibasic (SRD), and a hydroxyl-rich binder, sodium alginate (SA). During the sodiation of microsized SRD, cracks induced by volume expansion expose a new oxygen-rich surface, whereas the SA binder fills these cracks under pressure generated by volume expansion and binds the pulverized SRD together by hydrogen bonding between SRD and SA. Self-healing between hydroxyl-rich binder and oxygen-rich active material is a universal strategy for mitigating the pulverization-induced capacity decay of active materials, as demonstrated by the longer cycle life of the SRD electrode with other hydroxyl-rich binders, polyacrylic acid, and xanthan gum than with hydroxyl-free polytetrafluoroethylene binder.

INTRODUCTION
Sodium-ion batteries (SIBs) are promising energy storage devices because of the low cost and abundance of sodium resources. In the past decade, extensive efforts have been devoted to developing high-capacity electrodes in SIBs such as sulfur, phosphorus, tin, and organic materials. However, these high-capacity electrodes face a critical challenge because of the large volume change during sodiation and desodiation, and none of them can withstand such a large volume change. Therefore, the formation of cracks in microsized active materials gradually loses contact among particle-to-particle and partial-to-current collectors, leading to fast decay of capacity. Although the pulverization can be mitigated by minimizing the particle size to nanoscale, this increases the cost and reduces the volumetric capacity. Therefore, the development of a stable microsized high-capacity electrode is highly desired.

One promising way to alleviate the pulverization is to self-heal the cracks during cycling. Self-healing, which exists widely in biological systems, plays a critical role in curing mechanical injury of living organisms. It is a self-motivated process, which recovers the damage by living organisms without any external assistance. Inspired by biology, tremendous efforts have been devoted to mimicking self-healing chemistry. Recently, it was applied in a rechargeable battery to self-heal the cracks in battery electrodes.

The Bigger Picture
Self-healing between binder and active material is a promising strategy for overcoming the pulverization-induced capacity decay of high-capacity electrodes in Na-ion batteries. It requires the binder to have strong and reversible chemical bonding with the active material. Here, we report a hydrogen-bonding-based self-healing electrode consisting of a hydroxyl-rich sodium alginate binder and an oxygen-rich sodium rhodizionate dibasic active material. The strong and reversible chemical bonding between the binder and active material and the high pressure induced by large volume expansion drive the binder to fill the cracks induced by pulverization and self-heal these cracks upon cycling. The concept of self-healing between active material and binder in Na-ion batteries can be extended to other rechargeable batteries, thus providing an opportunity to develop high-energy batteries.
However, the cracks between binder and SnP$_3$ active material still grow continuously during cycling. Another way to self-heal the cracks is to use a self-healing binder, but it can only self-heal the cracks inside the binder and requires a large amount (>30 wt %) of binder to form a three-dimensional interconnected network to retain the integrity of the electrode. Therefore, current self-healing methods are not effective for extending the cycle life of high-capacity electrodes.

Self-healing between binder and active material is a promising strategy for high-capacity electrodes, but it is highly challenging because it requires the binder to have strong chemical bonding with active materials. For example, carboxymethyl cellulose (CMC) can bond to oxygen on the Si surface, improving the cycling stability of nano-Si. However, CMC is not effective for microsized Si because it cannot bond to the cracked Si because of the lack of oxygen on the fresh pulverized Si surface. Hydrogen bonds between biopolymer guar gum binder and silicon nanoparticles with average size of ~100 nm was reported; the silicon nanoparticles are not pulverized during cycling because they are less than 150 nm in size. However, even if the silicon particles are pulverized, the biopolymer guar gum binder cannot form hydrogen bonds with cracked silicon particles because no SiO$_x$ exists on the cracked Si surface. Self-healing of binder and active materials is essential for stable high-capacity electrodes but has never been explored. In this work, we demonstrate self-healing via hydrogen bonding between hydroxyl-rich binder and microsized oxygen-rich sodium rhodizonate dibasic (SRD). SRD (Figure 1A) has the highest oxygen content among organic electrode materials, and two of the four carbonyl groups in SRD can reversibly react with sodium ions, so there are still two carbonyl groups in fully sodiated SRD that can form hydrogen bonds with hydroxyl-rich binder at the fully sodiated state. Moreover, microsized SRD is pulverized during charge-discharge cycles. Hydroxyl-rich sodium alginate (SA) and hydroxyl-free polyvinylidene fluoride (PVDF) were selected as binders to demonstrate the role of self-healing between the hydroxyl group in the binder and oxygen on the surface of SRD. During the sodiation of SRD, the newly formed cracks expose a new oxygen-rich surface, whereas the SA binder with carbon black will fill these cracks under pressure as a result of the volume expansion of SRD and bind to oxygen on the surface of pulverized SRD to remain in electronic integration. The SA binder fills the cracks of the cycled SRD-SA electrode because of the hydrogen bond between SRD and SA, and high pressure from volume expansion of SRD, which is confirmed by scanning electron microscopy (SEM) images before and after cycling. The hydrogen bond between oxygen in pulverized SRD and the hydroxyl group in SA binder can integrate the pulverized micro-SRD together to alleviate the decay in capacity. The SRD electrodes with SA and PVDF binders exhibit similar charge-discharge behaviors, but the cycling stability of the SRD-SA electrode is much better than that of the SRD-PVDF electrode as a result of the self-healing effect. Therefore, self-healing between binder and active material paves the way for the development of high-capacity electrodes.

RESULTS AND DISCUSSION

SRD is an ideal model to demonstrate self-healing between electrode materials and binders. Firstly, microsized SRD suffers from severe pulverization as a result of the large volume change during charge-discharge cycles, and nanosized SRD can achieve better cycling stability. Secondly, SRD is insoluble in the electrolyte, as demonstrated by colorless electrolyte (Figure S1) after immersing the dark green SRD powder in the electrolyte for 24 hr. The SRD powder is at the bottom of the vial. In addition, Chihara et al. reported that sodiated SRD dissolves in the electrolyte.

1Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA
2Lead Contact
*Correspondence: cswang@umd.edu
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when charged to over 3.2 V, so sodiated SRD does not dissolve in the electrolyte in the cutoff window from 1.0 to 3.0 V. Thirdly, there are six oxygen atoms in a single SRD molecule, which can form strong chemical interactions via hydrogen bonds with hydroxyl groups in the binder (Figure 1B). Here, SA was selected as a binder because it contains two hydroxyl groups in each unit of the polymer architecture. The hydrogen bond is confirmed by Fourier transform infrared spectroscopy (FTIR) in Figure 1C. The strong and sharp absorption peak at ~1,450 cm\(^{-1}\) in the FTIR spectrum of SRD demonstrates the existence of carbonyl groups in SRD. A broad absorption peak at ~3,300 cm\(^{-1}\) represents O–H stretching vibrations from the hydroxyl group in SA binder. Two sharp absorption peaks at ~1,600 and ~1,400 cm\(^{-1}\) represent O–C–O asymmetric vibrations and symmetric vibrations from carboxylic groups in SA binder, respectively; the peak at ~1,300 cm\(^{-1}\) represents the deformation of pyranose rings. In the FTIR spectrum of SRD-SA film, most of the absorption peaks for SRD and SA are well maintained, but the deformation peak of pyranose rings at ~1,300 cm\(^{-1}\) for the SA binder disappears as a result of the hydrogen bonding between SRD and SA.\(^{27,28}\)
The morphology and structure of SRD is further characterized by X-ray diffraction (XRD), SEM, and Raman spectroscopy. The XRD pattern (Figure S2A) and SEM image (Figure S2B) demonstrate that SRD particles ~5 μm in size have a crystal structure with octahedron morphology. In the Raman spectrum (Figure S2C), the small absorption peak at ~300 cm⁻¹ and sharp absorption peak at ~350 cm⁻¹ represent sodium-oxygen vibrations, whereas the broad absorption band at 1,700 cm⁻¹ is indicative of vibrations of carbonyl groups in the SRD molecule. Therefore, XRD, SEM, and Raman results confirm the particle size and molecular structure of SRD.

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The electrochemical performance of SRD-PVDF and SRD-SA electrodes is measured in coin cells. The galvanostatic charge-discharge curves of the SRD-PVDF electrode at a current density of 50 mA g⁻¹ is shown in Figure 2A. In the first discharge, there are three plateaus, a long flat plateau at 2.0 V, a short plateau at 1.8 V, and a sloping plateau at 1.3 V. In the subsequent cycle, the long flat discharge plateau at 2.0 V
disappears, demonstrating that an irreversible phase transition process takes place in the first cycle. During the charge, there are four sloping plateaus at 1.8, 2.1, 2.35, and 2.6 V, corresponding to four discharge plateaus at 1.7, 2.05, 2.3, and 2.5 V. Similar charge and discharge behaviors are also observed in the SRD-SA electrode (Figure 2B). According to the theoretical calculations reported by Yamashita et al., SRD with space group Fddd reacts with two sodium ions step by step. 30 0.5 Na\(^+\) is inserted into the C\(_6\)O\(_6\) pair molecules during each reaction plateau, so the first discharge plateau at 2.5 V corresponds to the sodiation from Na\(_2\)C\(_6\)O\(_6\) to Na\(_2.5\)C\(_6\)O\(_6\), whereas the subsequent discharge plateaus at 2.3, 2.05, and 1.7 V refer to the formation of Na\(_3\)C\(_6\)O\(_6\), Na\(_3.5\)C\(_6\)O\(_6\), and Na\(_4\)C\(_6\)O\(_6\). The galvanostatic charge-discharge curves of SRD-PVDF (Figure 2A) and SRD-SA (Figure 2B) electrodes demonstrate that the sodiation-desodiation reaction of SRD is highly reversible after the first charge-discharge activation cycle. However, during the first discharge, the flat plateau of the SRD-SA electrode at 2.0 V is longer than that of the SRD-PVDF electrode, whereas the discharge plateau of the SRD-SA electrode at 1.3 V is shorter than that of the SRD-PVDF electrode, demonstrating that the hydrogen bonding between SRD and SA affects the electrochemical behavior. When sodium ions attack the oxygen in carbonyl groups during the first discharge, the hydrogen bond is dissociated. After the formation of a sodium-oxygen ionic bond, highly reactive free radicals are also formed in the benzene ring. 31 Because only two of the four carbonyl groups in SRD participate in the electrochemical reaction, the other two carbonyl groups still interact with SA binder via hydrogen bonds, which stabilizes the free radicals in the benzene ring; the free radicals formed in the SRD-PVDF electrode can react with each other freely, resulting in different electrochemical behavior to the SRD-SA electrode. To confirm the existence of hydrogen bonding between the carbonyl group of SRD and the hydroxyl group of SA binder upon cycling, we performed the FTIR measurements on pristine SA-SRD and SA-SRD electrodes after five activation cycles at 1 and 3 V. As shown in Figure S3, the FTIR peak of SA at \(~1,300\) cm\(^{-1}\) represents the deformation of pyranose rings in SA binder. In the FTIR spectra of pristine and cycled SRD-SA electrodes, the deformation peak of pyranose rings at \(~1,300\) cm\(^{-1}\) for the SA binder disappears as a result of hydrogen bonding between the carbonyl group in SRD and the hydroxyl group in SA. Moreover, the initial sodium insertion capacity of the SRD-PVDF electrode is higher than that of the SRD-SA electrode in Figure 2, probably because the interaction of hydrogen bonding between SRD and SA can hinder the sodiation process of SRD. Different behaviors (Figure S4) can also be observed in SRD-polyacrylic acid (PAA), SRD-xanthan gum (XG), and SRD-polytetrafluoroethylene (PTFE) electrodes, in which hydrogen bonding between SRD and SA, PAA, or XG affects the electrochemical behavior. The work reported by Liu et al. 23 discussed hydrogen bonding between guar gum binder and silicon nanoparticles. Their results also show that the hydrogen bonding enhances the capacity of a Si anode, and the guar gum binder contributes to the lower overpotential of the Si anode than of the SA binder. In the cyclic voltammogram (CV) of the SRD-PVDF electrode (Figure 2C), there is a strong and sharp peak at 1.88 V during the first cathodic scan, corresponding to the long flat discharge plateau at 2.0 V (Figure 2A). After the first cathodic scan, four pairs of redox peaks can be observed, coincident with the plateaus in the galvanostatic charge-discharge curves (Figure 2A). In the CV of the SRD-SA electrode (Figure 2D), a strong cathodic peak at 1.75 V appears during the first scan. It is 0.13 V lower than that of the SRD-PVDF electrode (Figure 2C), because the hydrogen bonding between SRD and SA enhances the strain caused by the initial sodiation, resulting in larger potential hysteresis. After the first cathodic scan, the cathodic and anodic peaks of the SRD-SA electrode are similar to those of the SRD-PVDF electrode. Therefore, the charge-discharge curves and CV manifest that the SRD-PVDF and
SRD-SA electrodes exhibit similar electrochemical behaviors, but the hydrogen bonding between SRD and SA does influence the electrochemical behavior of the SRD-SA electrode.

XRD, Raman, and FTIR spectroscopy were conducted to confirm the electrochemical reaction between SRD and Na ions. As shown in Figure S5A, the XRD pattern of a pristine SRD-SA electrode shows that the structure of SRD has the space group \textit{Fddd}. After discharge to 1.0 V, the XRD peaks of \textit{Fddd} SRD disappear, and a new sharp peak at 28.8° and a small peak at 31.7° appear, representing the formation of a new phase after sodiation. As predicted by the theoretical calculations, the new phase contains space group \textit{C2/m}, where \textit{C6O6} molecules in sodiated SRD are arranged pairwise.\textsuperscript{30} When the electrode is charged back to 3 V, the \textit{Fddd} structure of the pristine SRD is not recovered, but a new phase is formed, demonstrating the irreversible phase transition process in the first cycle. After 50 cycles, the newly formed crystal phase at the fully charged state is reversible and well maintained, further confirming that the irreversible phase transition process only exists in the first cycle. Raman spectroscopy was also carried out to investigate the reversible reaction mechanism of the SRD after five activation cycles. The Raman spectra in Figure S5B show that the pristine SRD in the electrode exhibits similar Raman peaks as the SRD powder. After sodiation to 1.0 V, the Raman peaks for stretching vibration and bending vibration of the carbonyl group at 1,550 and 440 cm\(^{-1}\) of SRD shift to 1,498 and 410 cm\(^{-1}\) as a result of sodiation of the carbonyl groups in SRD.\textsuperscript{32} After charged back to 3.0 V, all the Raman peaks for SRD are recovered, demonstrating the reversible reaction between SRD and sodium ions. Moreover, FTIR measurements for a pristine SRD-SA electrode and an SRD-SA electrode after five activation cycles further confirmed the sodiation reaction mechanism of SRD. As shown in Figure S5C, the strong and sharp absorption peak at 1,450 cm\(^{-1}\) for the carbonyl groups in SRD shifts to 1,396 cm\(^{-1}\) after discharge to 1.0 V as a result of the sodiation of the carbonyl group.\textsuperscript{32} After charged back to 3.0 V, all the FTIR peaks for SRD are recovered, demonstrating the reversible reaction between SRD and sodium ions. More importantly, both Raman and FTIR spectra show decreased peak frequency for the carbonyl group after sodiation as a result of the enhanced conjugation effect in sodiated SRD. The strong Raman and FTIR peaks for carbonyl groups after sodiation demonstrates the existence of carbonyl groups in sodiated SRD, confirming that only two of the four carbonyl groups in SRD participate in the sodiation reaction. Therefore, the XRD, Raman, and FTIR results illustrate that the reaction between SRD and sodium ions is reversible, except for the phase transition process in the first cycle.

The cyclic stability of SRD electrodes was further studied. Fluoroethylene carbonate (FEC) was added to the electrolyte to improve the performance of the SRD electrode. As demonstrated by our previous work, the electrode cycled in FEC-electrolyte exhibits a better cycle life than that in EC-electrolyte.\textsuperscript{12} As reported, FEC is reduced at a potential below 1.4 V versus Li/Li\(^{+}\), corresponding to 1.1 V versus Na/Na\(^{+}\).\textsuperscript{33} Hence, FEC is reduced in the potential range of 1.0–3.0 V versus Na/Na\(^{+}\) to build a stable solid electrolyte interphase (SEI) layer on the electrode during charge-discharge cycles.\textsuperscript{34,35} The stable SEI layer protects the structural integrity of the electrode. As shown in Figures S6A and S6B, SRD-SA electrodes with 10% and 20% SA binder exhibit similar charge-discharge curves as SRD-SA electrodes with 15% SA binder in Figure 2B; the long-term cycling test in Figure S6C shows that SRD-SA electrodes with 15% and 20% SA binder display similar cycling stability, and both of them are much better than that of electrode with 10% SA binder. Because SA binder improves the cycling stability but reduces the electrode capacity,
the SRD-SA electrode with 15% SA binder was selected for cyclic stability and rate capability tests. As shown in Figure 2E, the capacity of the SRD-SA electrode remains at 140 mAh g\(^{-1}\) after 500 cycles, with a slow capacity decay rate of 0.051% per cycle, whereas the SRD-PVDF electrode suffers from continuous capacity decay to 75 mAh g\(^{-1}\) after 500 cycles, with a high capacity decay rate of 0.118% per cycle. The Coulombic efficiency (CE) of the SRD-SA electrode is slightly lower than that of the SRD-PVDF electrode. To understand if the slightly lower CE of the SRD-SA electrode is induced by the self-healing process, the CE of SRD-SA electrodes with different content (15–30 wt %) of conductive carbon black was investigated because the amount of SEI is correlated to the amount of carbon in the electrodes. As shown in Figures S7A–S7C, the galvanostatic charge-discharge curves of SRD-SA electrodes with 15%, 20%, and 30% carbon black are similar to that of the SRD-PVDF electrode with 25% carbon black in Figure 2B, demonstrating that the content of carbon black does not affect the sodiation-desodiation reaction of SRD; a slightly higher capacity was observed in the SRD-SA electrode with high carbon content (Figure S7D) as a result of the improved electronic conductivity. The CE decreases with enhanced carbon black in the electrode, demonstrating that when SA binder with carbon black fills the newly formed cracks in the self-healing process of the SRD-SA electrode, the SEI is reformed. However, the CE of the SRD-SA electrode with 15% carbon black is close to 100%, which is even higher than that of the SRD-PVDF electrode. The better CE is ascribed to less pulverization as a result of strong bonding and less volume change caused by lower initial sodium insertion capacity of the SRD-SA electrode and the smaller amount of SEI as a result of the lower carbon content. Therefore, the CE of the SRD-SA electrode can be improved by optimizing the composition of the SRD-SA electrode. The superior rate capability of the SRD-SA electrode is also demonstrated in Figure 2F. When the current density increases from 20 to 1 A g\(^{-1}\), the capacity of the SRD-SA electrode only decreases from ~205 to ~102 mAh g\(^{-1}\), whereas the capacity of the SRD-PVDF electrode decreases from ~196 to ~52 mAh g\(^{-1}\). After the current density returns to 20 mA g\(^{-1}\), the capacity of the SRD-SA electrode can recover to 196 mAh g\(^{-1}\) immediately, whereas the capacity of the SRD-SA electrode can only recover to 156 mAh g\(^{-1}\). Therefore, the cycle life and rate capability results illustrate that the self-healing-enabled SRD-SA electrode exhibits superior electrochemical performance.

Cross-sections of the SRD-SA and SRD-PVDF electrodes before cycling and after 50 cycles are shown in Figure S8 to compare the thickness of the SRD-SA and SRD-PVDF electrodes before and after cycling. The thickness of the SRD-SA electrode before cycling is 24.3 μm as shown in Figure S8A, and it increases to 26.5 μm after cycling (Figure S8B) as a result of the volume expansion of SRD after cycling. In contrast, the thickness of the SRD-PVDF electrode enhances from 23.5 to 28.2 μm after cycling (Figures S8C and S8D), demonstrating more severe volume expansion of the SRD-PVDF electrode. This result confirms the volume expansion of the SRD electrode after cycling, and the self-healing between SRD and SA binder suppresses the volume expansion. In addition to the self-healing effect, the more severe volume expansion of the SRD-PVDF electrode is probably because of its higher initial sodium insertion capacity (Figure 2A) than that of the SRD-SA electrode (Figure 2B) and more residual sodium cations in the SRD-PVDF electrode as indicated by its lower initial CE in Figure 2E.

The hydrogen-bond-enabled self-healing mechanism was further confirmed by a sharp difference in the cycling stability of the SRD electrode with other hydroxyl-rich binders (PAA and XG) and another hydroxyl-free binder (PTFE). Both PAA and XG binders contain a hydroxyl group in each polymeric unit as shown in Figure S9.
The purpose of using PAA and XG binders is to demonstrate that the self-healing between oxygen-rich active materials and hydroxyl-rich binders is a universal strategy. SA was selected as a binder for detailed electrochemical characterization of the SRD electrode, because SA contains evenly distributed carboxylic groups in the polymer chain, resulting in better sodium-ion transportation in the vicinity of the SRD particle than XG, which contains a carboxylic group in the side chain of each polymeric unit rather than in the main polymer chain. Moreover, SA is much more polar than PAA and XG because of the formation of carboxylic salt in the alginate macromolecule, which can not only strengthen the interfacial interaction between binder and particle but also enhances the adhesion between the electrode layer and the Al substrate. Figure S4 shows the electrochemical behaviors of SRD with PAA, XG, or PTFE. SRD electrodes with PAA, XG, and PTFE binders show similar charge-discharge behaviors after first discharge (Figures S4A–S4C). However, the SRD-PTFE electrode suffers from rapid capacity decay in the initial 20 cycles, and only 22% of its initial capacity remains after 200 cycles, whereas the SRD-PAA and SRD-XG electrodes still retain ~70% of their initial capacity (Figure S4D). The significant difference in cycle life demonstrates that the self-healing strategy between oxygen-rich active materials and hydroxyl-rich binders is a universal strategy for oxygen-rich electrodes.

To demonstrate the self-healing mechanism, the morphology of the SRD-SA and SRD-PVDF electrodes before and after cycling was checked by SEM. In Figures 3A and 3B, pristine SRD-PVDF and SRD-SA electrodes consist of similar microsized octahedron particles. After 100 cycles, SRD particles with PVDF and SA binders are pulverized because of the large volume change (Figures 3C and 3D). In the SRD-PVDF electrode, cracks keep growing during cycling and eventually separate the pulverized SRD particles, resulting in continuous capacity decay. The magnified images (Figures 3C and S10A) show that there is no PVDF in the cracks of cycled SRD in the SRD-PVDF electrode. In contrast, the cracked SRD is still glued together by SA in the SRD-SA electrode. The magnified images (Figures 3D and S10B) show the existence of polymer inside the cracks. SA binder fills the cracks because of the high pressure induced by volume expansion and hydrogen bonds between SRD and SA. Hydrogen bonding plays a more important role because no PVDF was observed in the cracks with similar volume change. The SA binder in the cracks forms hydrogen bonds with SRD to bind the cracks together. The self-healing effect between SRD and SA binder heals the cracks and retains integrity of the electrode, resulting in exceptional battery performance. The surface of the SRD particles in the SRD-SA electrode is smooth except for cycled SRD particles. The hydrogen bonds on the surface of SRD-SA can absorb some nanoparticles derived from the pulverization during cycling, which to a certain extent indicates that SA has a strong bonding effect with SRD.

The self-healing process of the SRD-SA electrode is mimicked by pressing the SRD-SA film at 25 MPa to simulate the strain caused by the large volume change. High-capacity electrode materials such as Si particles initially form cracks on the surface and then pulverize because the large strain is generated by lithiation-induced expansion. Complete fracture results from the accumulation of large strain during particle expansion or contraction. The electrochemical pulverization of SRD is mimicked by the pressing experiment, because the pressing experiment can provide a large strain to fracture the SRD particles similar to the strain generated during particle expansion or contraction in the SRD electrode. Moreover, binder and carbon black are squeezed by the particle expansion or contraction during cycling and fill the cracks to combine the pulverized particles; the pressing experiment
also provides compression to the binder and carbon black, which is similar to the behavior in the SRD electrode. Therefore, the pressing experiment was used to mimic the electrochemical pulverization. The SRD particle is covered by SA binder in the pristine film (Figure 4A). After pressing under 25 MPa for 15 min, SRD particles were pulverized (Figures 4B and S11). However, SA binder is clearly observed in the cracks connecting the SRD pieces together, demonstrating that the SA binder does fill the SRD cracks under high pressure. Therefore, this result confirms the self-healing effect between SRD and SA binder.

The existence of polymer binder inside the crack is confirmed by Raman spectroscopy. To check whether polymer binder exists inside the crack, the laser beam is focused on two positions, a crack and nearby particle, for three samples (cycled SRD-SA electrode, pressed SRD-SA film, and cycled SRD-PVDF electrode). A shown in Figure S12A, when the laser beam is focused on the cracked particle in the cycled SRD-SA electrode, the resulting Raman spectrum is similar to that of SRD, demonstrating that the cracked particle is SRD. When the laser beam is moved to the crack, the Raman spectrum is similar to that of SA, which is direct evidence.
that there is SA inside the crack. A similar result is also observed for the pressed SRD-SA film in Figure S12B. The Raman spectrum for the crack is the same as for SA binder, confirming that SA binder exists inside the crack. For the cycled SRD-PVDF electrode (Figure S12C), no PVDF Raman peak is observed in the crack, instead, only small carbon peaks are found in the crack probably because of the carbon black underneath the cracked particle. Therefore, the Raman results confirm the existence of binder inside the cracks of the cycled SRD-SA electrode and pressed SRD-SA film.

The pressing tests for SRD-PVDF and SRD-PAA films were performed as a comparison with SRD-SA film. As shown in Figures S13A and S13B, both SRD-PVDF and SRD-PAA films consist of octahedron SRD particles surrounded by binders. After pressing under 25 MPa for 15 min, the SRD particles are pulverized in both films as demonstrated in Figures S13C and S13D. No binder exists in the gap between cracked SRD particles in the SRD-PVDF film, whereas binder is clearly observed in the cracks connecting the SRD pieces together in the SRD-PAA film, demonstrating that the PAA binder fills the SRD cracks under high pressure, but PVDF binder cannot fill the SRD cracks under high pressure. Therefore, this result further confirms the self-healing effect between oxygen in SRD and hydroxyl groups in binder.

The self-healing in the SRD-SA electrode is further confirmed by EIS evolution in the SRD-PVDF and SRD-SA electrodes. In Figure 5A, the interphase resistance of the SRD-PVDF electrode increases from ~310 to ~3,500 Ohm after 50 cycles as a result of particle pulverization. The pulverized particles lose contact with the current collector and conductive carbon, resulting in the increased interphase resistance. In contrast, the interphase resistance of the cycled SRD-SA electrode in Figure 5B decreases after cycling, because the self-healing effect maintains the conductivity of the cracked SRD microparticles, and the pulverization produces more surface area. The larger surface area of SRD particles enables better contact between the SRD particles and the electrolyte. Therefore, impedance analysis confirms the self-healing effect between SRD and SA binder.
Conclusion
In this work, we selected oxygen-rich SRD as a model electrode material to study self-healing between active material and binder. The SRD electrode with hydroxyl-rich SA, PAA, and XG binders exhibits better cycling stability than that with hydroxyl-free PVDF and PTFE binders as a result of the hydrogen-bonding-enabled self-healing effect. Hydrogen-bonding-enabled self-healing is a universal strategy to mitigate pulverization-induced capacity decay. The concept of self-healing between active materials and binders in SIBs can be extended to the other rechargeable batteries, thus providing an opportunity to develop high-energy batteries.

EXPERIMENTAL PROCEDURES
Material Characterizations
SEM images were taken with a Hitachi SU-70 analytical ultra-high resolution SEM (Japan); XRD patterns were recorded on a Bruker Smart1000 (Bruker AXS, USA) with CuKα radiation; Raman measurements were performed on a Horiba Jobin Yvon Labram Aramis with a 532 nm diode-pumped solid-state laser, attenuated to give ~900 μW power at the sample surface. FTIR was recorded on a NEXUS 670 FT-IR Instrument.

Electrochemical Measurements
SRD was mixed with carbon black and SA, PAA, XG, PVDF, or PTFE binder to form a slurry at a weight ratio of 60:25:15. The electrode was prepared by casting the slurry
onto aluminum foil with a doctor blade and drying in a vacuum oven at 100°C overnight. The slurry coated on aluminum foil was punched into circular electrodes with an area mass loading of ~1.5 mg cm⁻² and electrode density of ~0.49 g cm⁻³. Coin cells for SIBs were assembled with sodium metal as the counter electrode, 1 M NaClO₄ in a mixture of fluoroethylene carbonate, ethylene carbonate, and dimethyl carbonate (FEC/EC/DMC at 2:3:5 by volume), and Celgard 3501 (Celgard, USA) as the separator. Electrochemical performance was tested with an Arbin battery test station (BT2000, Arbin Instruments, USA). Cyclic voltammograms were recorded with Gamry Reference 3000 Potentiostat/Galvanostat/ZRA with a scan rate of 0.1 mV s⁻¹. Impedance analysis was also performed by Gamry Reference 3000 Potentiostat/Galvanostat/ZRA.

SUPPLEMENTAL INFORMATION

Supplemental Information includes 13 figures and can be found with this article online at https://doi.org/10.1016/j.chempr.2017.09.004.

AUTHOR CONTRIBUTIONS

C.L. and C.W. conceived and designed the experiments. C.W. directed the project. C.L., X.F., Z.M., and T.G. performed the battery assembly and characterization experiments. All authors discussed and analyzed the data. C.L. wrote the first draft of the manuscript. All authors discussed the results and commented on the manuscript.

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REFERENCES AND NOTES


35. Markевич, E., Salitra, G., and Aurbach, D. (2017). Fluoroethylene carbonate as an important component for the formation of an effective solid electrolyte interphase on anodes and cathodes for advanced Li-ion batteries. ACS Energy Lett. 2, 1337–1345.