

Three-Dimensional Conductive Gel Network as an Effective Binder for High-Performance Si Electrodes in Lithium-Ion Batteries

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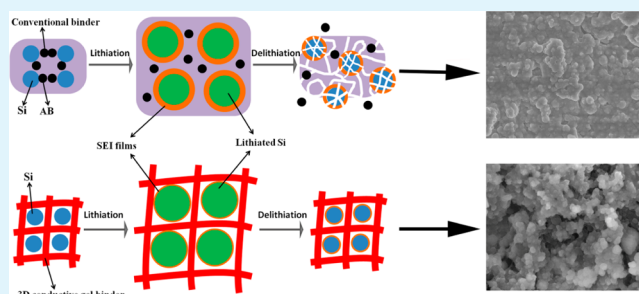
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S Supporting Information

ABSTRACT: Silicon (Si) has been widely investigated as a candidate for lithium-ion batteries (LIBs) due to its extremely high specific capacity. The binders play a key role in fabricating high-performance Si electrodes which usually suffer from the huge volume expansion associated with the alloying and dealloying processes. Here we develop a facile route to prepare a three-dimensional (3D) conductive interpenetrated gel network as a novel binder for high-performance Si anodes through chemically cross-linking of acrylic acid monomer followed by the in situ polymerization of aniline. The excellent electrical conductivity, strong mechanical adhesion and high electrolyte uptake render the conductive gel network a potential binder for high-performance Si anodes. The resultant Si anodes exhibit excellent cycling stability, high Coulombic efficiency and superior rate capability, revealing better electrochemical properties compared to the Si anodes with conventional binders. The 3D conductive gel binder could not only accommodate the volume expansion and maintain electric connectivity, but also assist in the formation of stable solid electrolyte interphase (SEI) films. Such a strategy sheds light on the design of polymer binders in LIBs, especially for high-capacity electrode materials with huge volume changes during long-term cycling.

KEYWORDS: lithium-ion batteries, conductive gel network, silicon anode, polymer binder, electrochemical performance



1. INTRODUCTION

As there is an ever-increasing demand of energy storage for rapidly growing industrial fields from portable electronics to energy storage systems, lithium-ion batteries (LIBs) are requested to afford higher energy densities with excellent electrochemical properties.^{1,2} Although graphite has been utilized as anode materials in most commercial LIBs, it suffers from low specific capacity (370 mAh g⁻¹) and safety issues.^{3,4} Because of the ultrahigh theoretical capacity (4200 mAh g⁻¹), relatively low discharge potential, environmentally benign, low cost and abundance in nature, Silicon (Si) has become one of the most potential substitutes to take the place of traditional graphite anode.^{5–8} However, the practical applications of Si anode are severely constrained by the huge volume expansion during the lithiation/delithiation processes, which results in severe particle pulverization and excess growth of solid electrolyte interphase (SEI), leading to rapid degradation of the electrode and short cycle life upon cycling.^{9–11}

Tremendous efforts have been concentrated on the development of Si active materials to accommodate the above issue, mostly through nanostructured material design.^{12,13} Nevertheless, these methods are usually complicated, high cost, and not environmentally benign.¹⁴ In contrast, the binder, which holds electrode particles together onto the current collectors, has attracted less attention. The binder is believed to play a key role in preparing high-performance electrodes as it maintains

the mechanical and electronic integrity of the electrode.¹⁵ A good battery binder for Si anode should be able to provide strong chemical interactions with the active materials instead of weak van der Waals forces to tolerate the huge volume expansion during long-term cycling. Several research groups have proposed different candidates of new binders to enhance the interaction of Si and binder, such as carboxymethyl cellulose (CMC),¹⁶ poly(acrylic acid) (PAA),¹⁷ alginate,¹⁸ and carboxymethyl chitosan,¹⁹ each of which exhibited better binding performance than the conventional polyvinylidene fluoride (PVDF) binders. However, it is still weak physical interactions among the binder chains and the one-dimensional (1D) structure of the binder is susceptible to sliding upon the sustaining volume expansion of Si. Consequently, an innovative strategy to develop three-dimensional (3D) cross-linked binders is proposed, through which the 3D interconnected network provides robust chemical interactions between the binder chains. For instance, the calcium-mediated cross-linked alginate hydrogels and some hybridized networks have been proposed as novel binders for Si and Si-based anodes.^{20–24} Other strategies of fabricating self-healing polymer through supramolecular interactions were also adopted for Si bind-

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er.^{25,26} These 3D cross-linked designs significantly improved the electrochemical performance of Si. Recently, Wang et al. proposed an interpenetrated PAA–PVA superabsorbent gel binder for Si anodes, which could effectively alleviate the huge volume expansion during cycling due to the strong adhesion of the transformable network.²⁷ Though notable improvements in the electrochemical performance have been accomplished, the conductivity of the gel polymer binders is still restricted by the insulating polymer chains, which could greatly hinder the electron transportation. To form conducting bridges between the active materials, a relatively high content of carbonaceous conducting agents without any capacities and binding forces such as acetylene black (AB), has to be added. These conductive additives tend to be pushed away from the Si anodes by large volume change during lithiation/delithiation processes, leading to broken electric connections and increased resistance of the electrode, consequently decreasing the electrochemical performance of the anodes.^{28–30} To optimizing the electronic conductivity of gel polymer binder, a meaningful route is to introduce a conducting polymer into the common gel binder systems, which could not only eliminate the utilization of conductive additives and increase the electrode capacity, but also help to keep the electrical conductivity and structural integrity of high-performance Si electrodes.

Polyaniline (PANI) is considered as an appropriate candidate owing to its facile synthesis, high conductivity, and environmental stability, thus it has attracted great attention in the manufacturing of high-performance Si anodes in recent years.^{31,32} Herein, we present a convenient route to prepare a 3D conductive PAA/PANI interpenetrating polymer network (IPN) as a novel binder for high-performance Si anodes. The network of PAA hydrogel was synthesized by chemically cross-linking of acrylic acid (AA) monomer, and then aniline (ANI) solution was absorbed and in situ polymerized into the PAA network; thus, the PAA/PANI IPN binder was obtained. This 3D conductive gel could not only restrict the huge volume expansion of Si during continual cycling, but also promote the transport of both electrons and ions to form continuous conducting bridges between active materials and binders. All these help to keep the electrical conductivity, structural integrity, and the SEI film stability, thus significantly improve the electrochemical performance of the Si anode. Using the PAA/PANI IPN as a novel binder, the Si electrode exhibits superior cycling performance and rate capability, indicating that this facile strategy is a promising route for energy storage applications.

2. RESULTS AND DISCUSSION

The schematic of the synthesis of the 3D conductive PAA/PANI IPN binder for Si anodes is shown in Figure 1. In an aqueous solution, the AA monomers underwent chemically cross-linking through NMBA, resulting in a hydrogel network.^{33,34} Simultaneously, the hydrogen bonds were formed between the carboxylic acid groups of PAA network and the hydroxyl groups of SiO₂ on the surface of the Si, which is beneficial to the stability of Si anodes. When ANI monomers were penetrated into the Si/PAA hydrogel and in situ polymerized, PANI chains were formed inside of hydrogel owing to the porous network structure. Cation radicals (–NH₃⁺), which were generated during the oxidation of the ANI monomers at the beginning of the polymerization, were absorbed into the pores of PAA network owing to their strong electrostatic interactions with anion radicals (–COO[–]). During

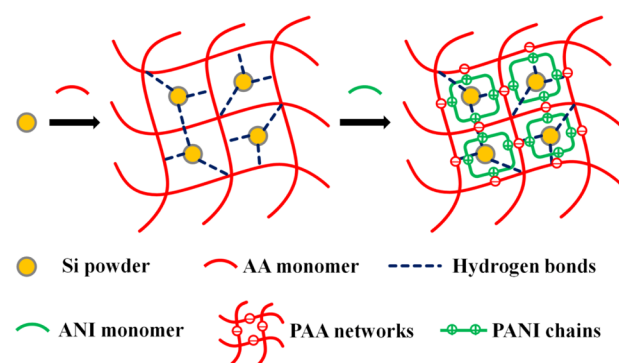


Figure 1. Schematic illustration of the formation process of the 3D conductive PAA/PANI IPN binder for Si anodes.

synthesis, the conducting PANI chains (containing –NH₃⁺) were inclined to integrate with the PAA networks (containing –COO[–]) via physical or chemical interaction, which resulted in the formation of an interpenetrating network structure. The SEM image of the as-prepared PAA/PANI IPN binder was shown in Figure S1. As can be seen, the hydrogel displays a porous network structure. This 3D conducting network offers excellent mechanical strength and electrical conductivity, and thus can serve as a robust matrix to accommodate the volume expansion as well as a highway for Li⁺/electron transport.

Fourier Transform infrared spectroscopy (FTIR) studies were conducted to confirm the chemical structure of the interpenetrating network, as shown in Figure S2 in the Supporting Information. In the FTIR spectrum of the commercial Si, the band at about 1121 cm^{–1} is assigned to Si–O, indicating the formation of the SiO₂ layer in pristine Si, which agrees with previous reports.^{22,27} For PAA, the absorption band at 1710 cm^{–1} is attributed to C=O stretching, 1472 and 1391 cm^{–1} are the results of C=O bending in –COOH and –COO[–] groups, respectively.^{33,35} The PAA/PANI IPN shows similar FTIR spectrum as PAA except for the appearance of some new peaks. The peaks at 1570 and 1490 cm^{–1} are responsible for the stretching vibration of quinoid ring and benzenoid ring in PANI.³¹ Besides, the weakening of band intensity at 1710 and 1391 cm^{–1}, and the disappearance of 1472 cm^{–1} band reveal strong hydrogen bonds between PAA and PANI, which is benefit for the stability of the conductive hydrogel.^{33,36} Moreover, the stretching vibration peak of C=O in the Si–PAA/PANI IPN becomes wider at a higher wavenumber (1725 cm^{–1}), indicating a chemical interaction between PAA/PANI IPN and Si, which increased the structural integrity of Si anode during lithiation and delithiation processes.³⁷

Figure 2 shows the details of the Si anode materials. The Scanning Electron Microscopy (SEM) image of the commercial Si powders shows that the Si used in this study is elliptical or spherical in shape with the average particle size about 200 nm and prone to aggregation, as shown in Figure 2a. Figure 2b shows the X-ray diffraction (XRD) pattern of the Si nanoparticles. The peaks located at 27.7, 46.6, 55.4, 68.5, and 75.8° can be indexed to the cubic Si phase (JCPDS Card no. 01–0787), which are assigned to the (111), (220), (311), (440), (331) lattice planes, respectively. The peaks are sharp, indicating the good crystallinity and high purity of the Si powders. The SEM images of the Si electrode prepared with the conductive PAA/PANI IPN binder are presented in Figure 2c, d, in which the weight ratio between Si and the binder was

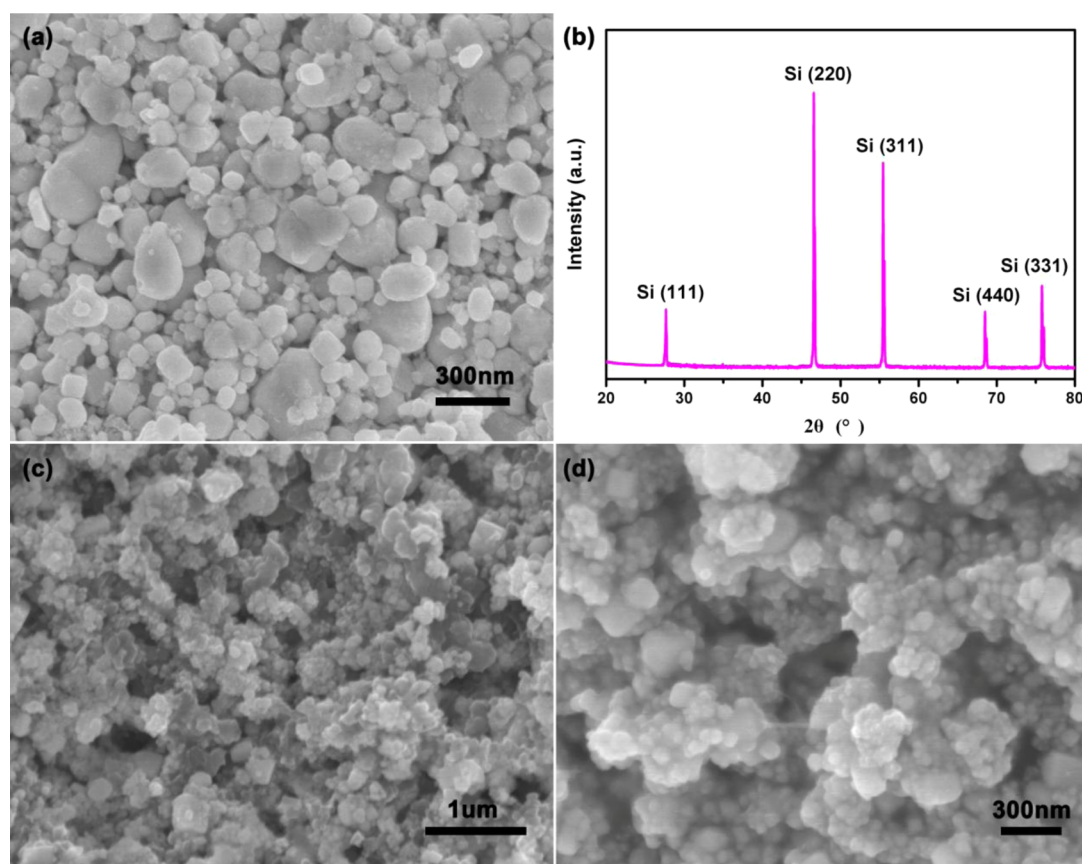


Figure 2. (a) SEM image of Si before fabrication, (b) XRD diffraction of Si, (c, d) SEM images of Si-PAA/PANI IPN electrode (Si:binder = 60:40, wt %).

controlled at 60:40. As can be seen, the electrode exhibits a porous architecture. These microsized pores can not only accelerate liquid electrolyte diffusion into the electrode but also offer free space to accommodate the huge volume change of the Si particle, thus significantly improving the electrochemical performance.

The electrical conductivity of the PAA/PANI IPN binder was measured via four-probe method, as shown in Figure S3 in the Supporting Information. Different PANI content in the binder could be obtained through modulating the concentration of monomers during polymerization. The electrical conductivity increases with increasing the content of PANI and encounters bottleneck and reverse as the PANI content reaches 20 wt %, which is because that only part PANI can be absorbed into the PAA network due to its osmosis character. The saturated electrical conductivity is about $1.25 \times 10^{-2} \text{ S cm}^{-1}$, indicating the good conductivity of the gel binder.

Except for the inherent electrical conductivity, the strong adhesion property is another essential requirement for an ideal battery binder.^{14,38} The conventional peeling tests were conducted to quantitatively investigate the binder effect on the adhesion strength of the electrode films. As can be seen in Figure S4 in the Supporting Information, the Si-PVDF and Si-PAA films exhibit small initial peel-off workloads ($\sim 2 \text{ N}$ for Si-PVDF, $\sim 7 \text{ N}$ for Si-PAA). By contrast, the Si-PAA/PANI IPN film exhibits much higher initial peeling force ($\sim 16 \text{ N}$), as a robust network structure is supposed to significantly strengthen the mechanical binding force and enhance the particle/particle cohesion strength. Tight association of the Si with the conductive binder affords better and lasting electric conduction

in the electrode, which assures the physical integration of the electrode.³⁹

Besides, the Li^+ transportation efficiency is vital to accomplish the full capacity of the high-capacity Si anodes.⁴⁰ The swelling test was carried out to evaluate the electrolyte uptake in different binders, as shown in Figure S5 in the Supporting Information. In the PAA/PANI IPN binder system, the electrolyte uptake is accounting for about 23% of its final weight in 20 h, much higher than that of PVDF (11%) and PAA (14%). Moreover, it shows a faster wetting rate compared with other binders. The high electrolyte uptake and fast wetting rate of the PAA/PANI IPN binder can be attributed to the porous network structure, which allows fast electrolyte impregnation and high Li^+ transportation efficiency, beneficial for improving the electrochemical performance of Si anode.

To investigate the electrochemical performance of Si electrodes with different binders, we fabricated coin-type half-cells with Li metal as both reference and counter electrodes for a series of galvanostatic measurements. Figure 3a shows the first galvanostatic profiles at a current density of 420 mA g^{-1} (0.1 C) for the Si electrodes with different binders. All three electrodes exhibit similar plateau profiles at 0.1 V for lithiation and 0.45 V for delithiation, consistent with the behavior of crystalline Si.^{41,42} The sloping part existing from 1.0 to 0.4 V is attributed to the formation of the SEI layer. During this process the electrolyte are reduced on the surface of electrode, leading to the irreversible capacity loss.^{10,24} The Si/PAA/PANI IPN electrode shows a higher initial Coulombic efficiency of 89.3% as compared with 72.6% and 79.4% for the electrodes with PVDF and PAA, respectively, indicating that the 3D conductive

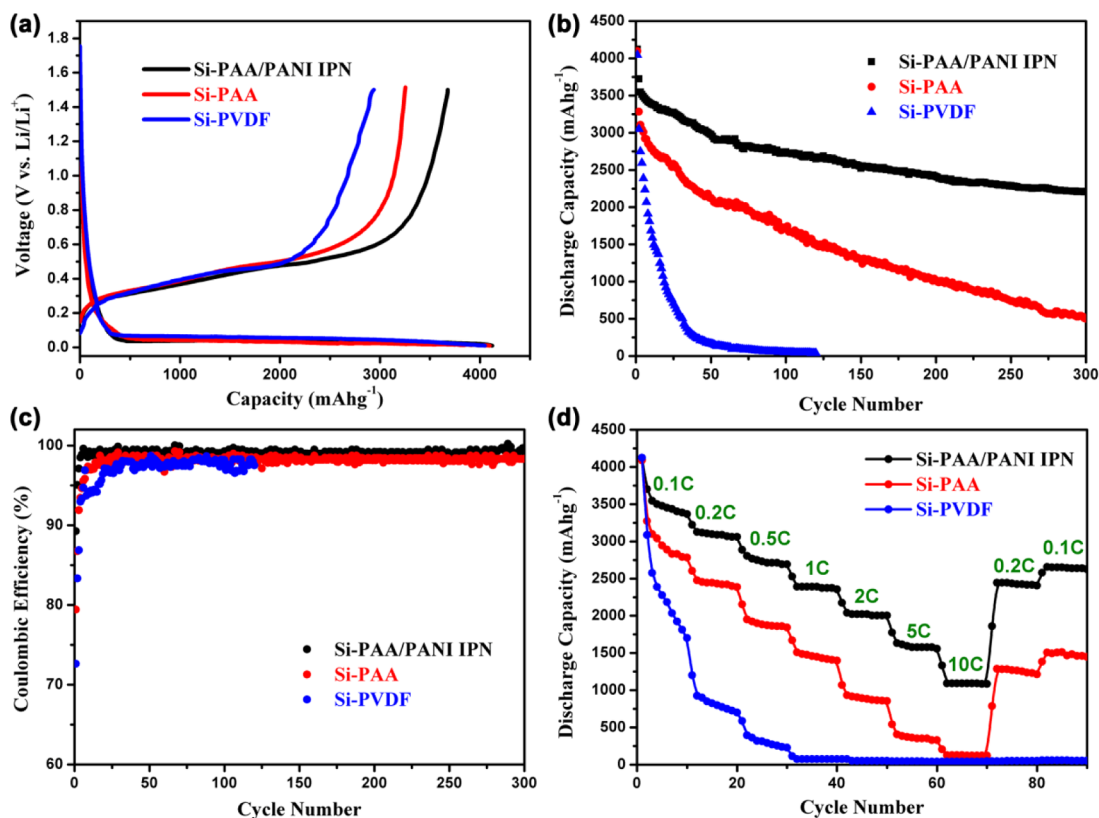


Figure 3. (a) Initial charge/discharge voltage profiles, (b) cycling performance, (c) Coulombic efficiency, and (d) rate performance of the Si anodes using different binders.

gel network could promote the reversibility during the first lithiation/delithiation by forming a relatively stable SEI layer. The improved reversibility is also reflected in the subsequent cycles. Figure 3b, c shows the cycling stability and Coulombic efficiency of Si anode using different binders. For Si/PDVF electrode, the capacity rapidly dropped to almost zero, which can be ascribed to the weak van der Waals forces between Si and the binder which cannot alleviate the huge volume expansion upon cycling. Though the Si anode with functional PAA binder shows a better cycling performance (505.3 mAh g^{-1} after 300 cycles), it cannot endure the repeated mechanical stress during long-term cycles. In contrast, the Si anode with PAA/PANI IPN binder shows a high capacity of 2205 mAh g^{-1} after 300 cycles with a high Coulombic efficiency above 99%. The high Coulombic efficiency demonstrates that the SEI layers are stable, thus reconfirming the role of the 3D conductive gel network structure for long-term cycling stability. The 3D conductive gel binder also contributes to the notably improved rate performance of Si electrode, as shown in Figure 3d, the Si-PAA/PANI IPN electrode retains its stable cycling stability at various rates. Even at a high current of 10 C, a specific capacity of $1091.4 \text{ mAh g}^{-1}$ is achieved and the capacity quickly returns to $2644.6 \text{ mAh g}^{-1}$ when the current was changed back to 0.1 C. By contrast, both the Si/PVDF and Si/PAA display a worse rate performance due to their severe capacity decay with cycling. The outstanding electrochemical performance achieved by using a 3D conducting gel network binder is ascribed to the maintenance of mechanical integrity and electric contact of the electrode, suggesting that the PAA/PANI IPN could be a promising binder for high specific capacity Si-based anode in LIBs.

To further investigate the reasons of the improved cycle performance and rate capacity of the Si-PAA/PANI IPN anode, we conducted the electrochemical impedance spectra (EIS) of the electrodes with different binders after 100th cycling at the fully delithiation state. As can be seen in Figure 4, all the

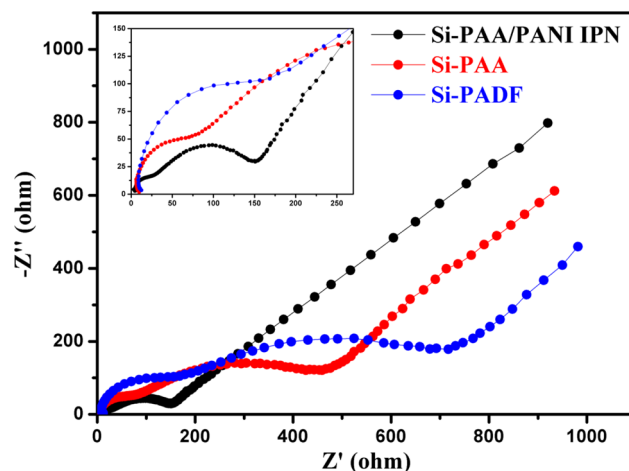


Figure 4. EIS spectra of the Si anodes with different binders after 100 cycles.

impedance plots can be divided into one depressed semicircle in the high frequency region which reflected the resistance of the SEI film (R_{SEI}), one semicircle in the middle frequency region which was attributed to the charge-transfer resistance (R_{ct}), and one sloping line in the low frequency region which stood for the Warburg impedance.^{43–45} Obviously, the arc of

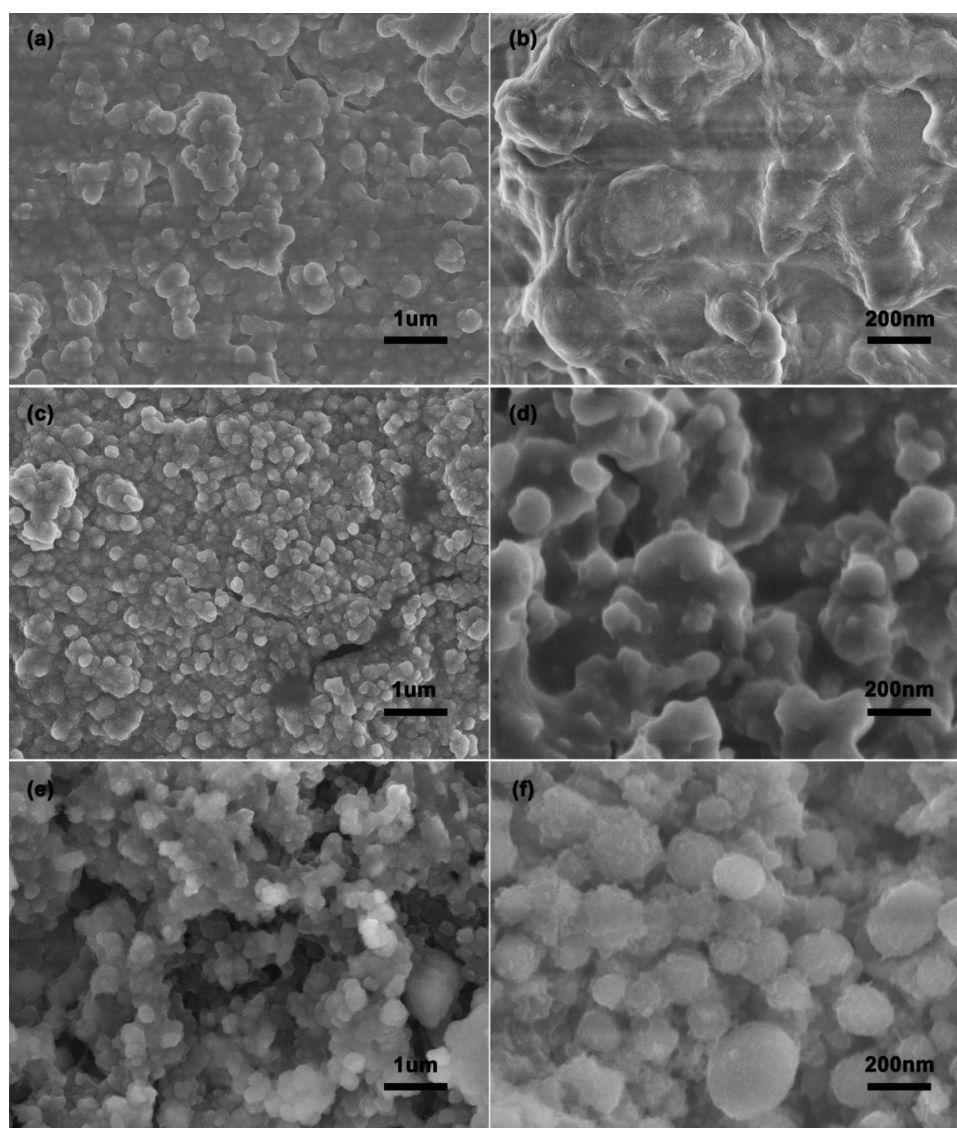


Figure 5. SEM images of (a, b) Si-PVDF electrode, (c, d) Si-PAA electrode, and (e, f) Si-PAA/PANI IPN electrode after 100 cycles with different magnifications.

the Si-PAA/PANI IPN electrode exhibits a much smaller radius compared to other electrodes, indicating the smaller R_{SEI} and R_{ct} . This result demonstrates that the 3D conducting porous gel network binder could not only stabilize the SEI layer by accommodating the large volume expansion of Si, but also improve the charge transfer rate during charge/discharge processes by enhancing the electrical conductivity and facilitating the penetration of the electrolyte, thus resulting in a significant improvement in the electrochemical performances.

The SEM images of the Si electrodes with different binders after long-term cycling are shown in Figure 5. In both Si-PVDF and Si-PAA electrodes, severe cracks are observed (Figure 5a, c) and the Si particles are completely pulverized after 100 cycles (Figure 5b, d). By contrast, the Si-PAA/PANI IPN electrode still preserves its uniform particle distribution and only slight cracks can be observed after 100 cycles (Figure 5e). Meanwhile, the spherical shapes of Si particles are still individually visible and the porous structure of the electrode are well preserved (Figure 5f), indicating the better electrode integrity upon deep galvanostatic cycling.⁴⁶

The enhanced structural integrity and electrochemical performance based on the 3D conducting network gel binder is illustrated in Figure 6. In a conventional Si electrode with 1D nonconductive binder, the substantial volume expansion of Si during cycling would cause the pulverization of the electrode and the destruction of electrical contact between the Si active materials and the current collector. Besides, the SEI film formed during cycling would break due to the large volume change and regenerate on newly exposed surfaces, resulting in the degradation of the electrode integrity and rapid capacity loss.⁴⁷ On the contrary, the 3D conductive gel binder could have obvious advantages sustaining the volume expansion and slow down the electrode pulverization due to the porous structure, which would assist in constructing a stable SEI film for Si anodes. Moreover, the SEI film could be formed on the surface of the PAA/PANI IPN binder rather than on the Si surface directly owing to its good electric conductivity, which effectively reduces the degree of the repeated formation/decomposition of SEI film. Hence the thinner SEI layers with better stability would be formed, leading to the outstanding

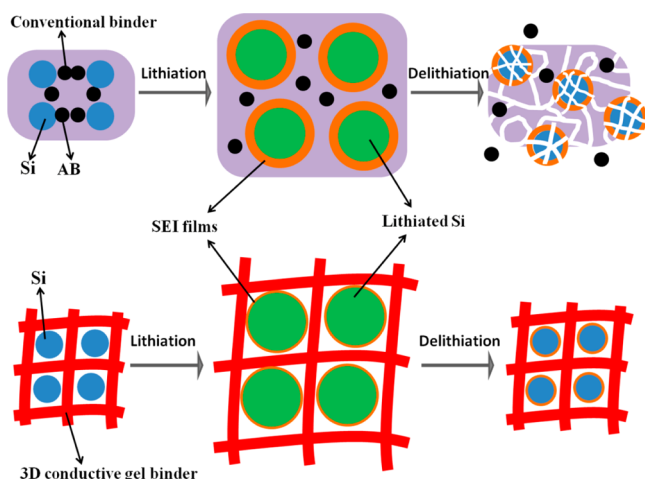


Figure 6. Schematic illustration of the Si electrodes in the process of Li^+ insertion and extraction using different binders.

cycling stability with a high Coulombic efficiency over 99% during long-term cycling, as mentioned before (Figure 3c).

3. CONCLUSIONS

In summary, we have developed a 3D conductive interpenetrated gel network as a promising binder for high-performance Si anodes via a facile in situ polymerization route of aniline into the PAA hydrogel network. By taking advantages of 3D porous structure, strong chemical binding adhesion, as well as favorable electrical conductivity, the gel binder can efficiently alleviate the huge volume expansion of Si and maintain electric connectivity simultaneously. Meanwhile, this designed binder can also enhance the stability of the SEI layer formed on the surface of Si over long-term cycling. As a consequence, the Si anodes with the 3D conductive gel binder exhibit high capacity and Coulombic efficiency, excellent rate capability, favorable charge-transfer rate and superior electrode integrity. Considering all of the advantages, it is believed that this 3D conductive interpenetrated gel binder has a great chance to be applied for Si-based anodes in LIBs, as well as for other high-capacity electrodes with severe volume expansions during the long-term charge/discharge process.

■ ASSOCIATED CONTENT

Supporting Information

Details about experimental methods, images of SEM photo, FTIR spectra, electrical conductivities, adhesion measurements, and swelling tests. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04058.

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Notes

The authors declare no competing financial interest.

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