


Conductive, Stretchable, and Self-healing Ionic Gel Based on Dynamic Covalent Bonds and Electrostatic Interaction

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 Electronic Supplementary Information

Abstract Integrating multiple functions into one gel that can be widely applied to electronic devices as well as chemical and biomedical engineering remains a big challenge. Here, a multifunctional ionic liquid/dynamic covalent bonds (ionic/DCB) type gel was designed and synthesized *via* one-pot polymerization. With the assistance of electrostatic interaction provided by the imidazolium cations of IL and the reversible DCB of boronic ester, as-prepared ionic/DCB gel showed good stretchable properties and high ionic conductivity at ambient conditions. In addition, the electrostatic interaction between imidazolium cations and sulfonate anions and the reversible DCB led to enhanced chain mobility and thereby excellent self-healing properties. Particularly, sulfonate anions in ionic/DCB gel could alleviate the migration of electronegative polysulfide and promote the transportation of electropositive lithium ion in lithium-sulfur battery system. Therefore, this work provides a new insight to promote the current research on self-healing gels, hopefully expanding their applications in electronic devices.

Keywords Ionic gel; Conductivity; Self-healing; Dynamic covalent bonds; Lithium-sulfur battery

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INTRODUCTION

Self-healing is one of the most significant properties that enable a material to intrinsically cure wounds.^[1–4] During the past decade, self-healing materials based on noncovalent, such as electrostatic interactions,^[5] ionic bonding,^[6,7] hydrogen bonding,^[8,9] metal-ligand coordination,^[10,11] host-guest interactions,^[12,13] and/or dynamic covalent interactions (phenylboronate esters,^[14,15] disulfide^[16,17] or acylhydrazone bond^[18]) have been investigated and applied for electronic skin,^[19] supercapacitors,^[20] lithium ion batteries,^[21] and heat sensors.^[22] For example, Yang *et al.* prepared a physically cross-linked hydrogel *via* hydrogen and dual metal-carboxylate coordination bonds. The obtained hydrogel showed good mechanical strength and self-healing properties.^[23] Wei and co-workers synthesized a highly stretchable and self-healable hydrogel. The resulting hydrogel exhibited high robustness and good cohesiveness due to the electrostatic interaction.^[24] Jiang *et al.* prepared a hydrogel based on agarose/PVA double network *via* a dynamic boronic ester bond. As a result, the hydrogel possessed ultrafast self-healing properties even in the water.^[25] Self-healing is a process of polymer chain

recombination, which requires re-bonding of chains to their original conditions. However, conventional hydrogels are unable to efficiently accomplish self-healing at room temperature because of relatively weak molecular chain mobility of polymers. It remains challenging to develop novel polymer gels with excellent self-healing properties in an effective way.

Ionic liquids (ILs) are a type of cation/anion pairs with melting temperature below 100 °C. They have attracted much attention due to their unique properties, such as negligible vapor pressure, high conductivity, high thermal stability, and a wide electrochemical stability window. Poly(ionic liquid)s (PILs) are polymerized ILs that consist of a polymeric backbone and an IL species in monomer repeating units.^[26–30] More recently, PIL-derived self-healing materials have been investigated by several groups.^[31,32] The electrostatic interactions between the organic cations and counteranions act as the driving force to cure polymers. In addition, when ionic groups in a polymer matrix aggregate and form multiplets and clusters sequentially, they could be recombined in a short relaxation period after crack damage. Therefore, the ionic aggregate structure possesses self-healing feature to a certain extent.^[33]

Herein, imidazolium-type ionic liquid/dynamic covalent bonds (ionic/DCB) gels with tunable autonomous self-healing capability were synthesized by co-polymerization of 4-

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vinylphenylboronic acid (4-VPBA) and lithium 2-acrylamido-2-propane-1-sulfonate (AMPSLi) in 3-(1,2-dihydroxypropyl)-1-methylimidazole chloride (DDPMIMCl) (Fig. S1 in the electronic supplementary information, ESI). The electrostatic interactions between imidazolium cations and sulfonate anions and the dynamic boronic ester endowed the ionic/DCB gels with good self-healing properties and high ionic conductivity. Moreover, polymer gels based on sole electrostatic interaction (ionic gel) and dynamic covalent bonds (DCB) gel were also prepared for comparison. Furthermore, the prepared ionic/DCB gel showed potential in lithium-sulfur battery.^[34,35]

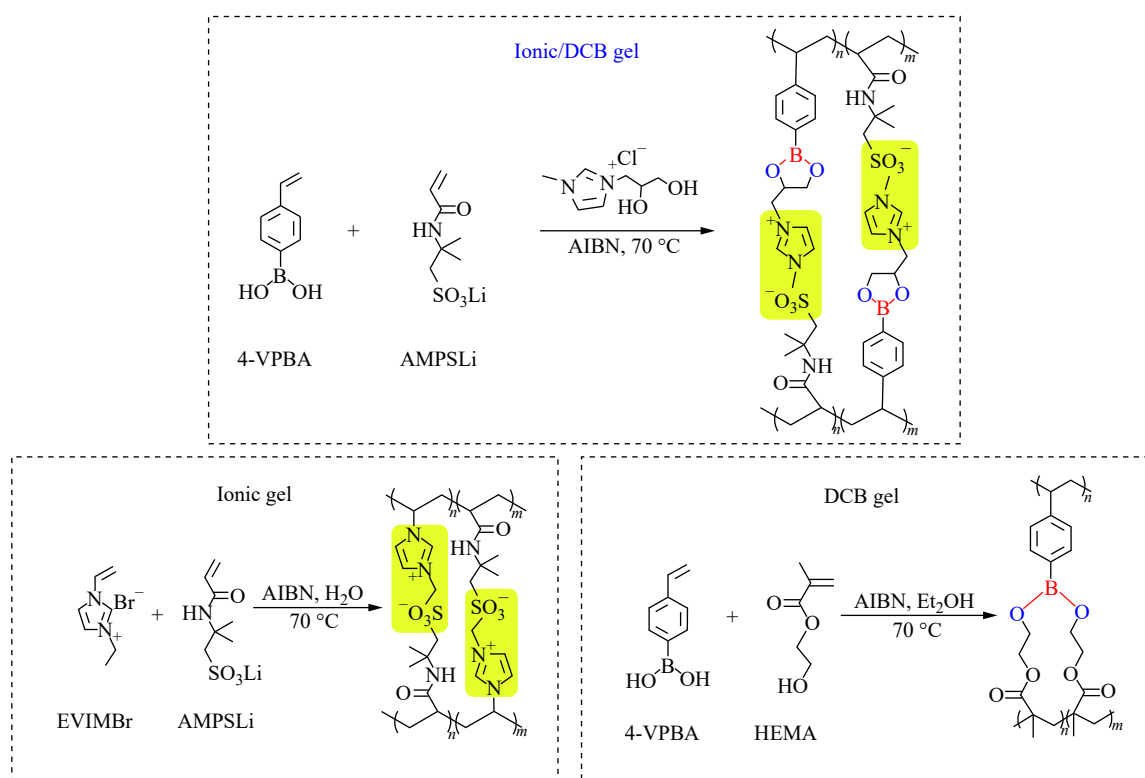
RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route for the preparation of three types of gels. Ionic/DCB gels were prepared *via* co-polymerization of 4-VPBA and AMPSLi, in which an IL, DDPMIMCl, was used as the bridged linkage (Fig. S2 in ESI). Ionic gels were prepared *via* co-polymerization of an IL monomer, 3-ethyl-1-vinylimidazole bromide (EVIMBr), and AMPSLi, in which IL was used as the co-monomer. DCB gels were prepared *via* co-polymerization of 4-VPBA and hydroxyethyl methylacrylate (HEMA), without the IL units.

The chemical structure and purity of all the polymeric gels were confirmed by Fourier transform infrared (FTIR) spectra (Fig. S3 in ESI). It can be seen that the broad and strong absorption band at 3351 cm^{-1} is attributed to the stretching vibration of $-\text{OH}$ and $-\text{NH}$ group,^[36] and the absorption bands centered at $2922\text{--}2861\text{ cm}^{-1}$ are attributed to the

$-\text{CH}_3$ (stretching) and $-\text{CH}_2$ (stretching) vibrations. Typical absorption bands of $-\text{COO}$ and $-\text{CONH}$ are observed at 1729 and 1665 cm^{-1} , respectively. Both ionic/DCB and ionic gels show a characteristic band at 1548 cm^{-1} due to the stretching vibration of imidazolium ring.^[37] The bands at 1435 and 655 cm^{-1} correspond to the asymmetrical stretching vibration and bending vibration of $\text{B}-\text{O}$, respectively, indicating the formation of boronic ester groups in ionic/DCB and DCB gels.^[38] In addition, the band of 1100 cm^{-1} representing $-\text{SO}_3^-$ groups can be observed in both ionic/DCB and ionic gels.^[39] The results of FTIR spectra confirmed the successful preparation of three kinds of gels.

The boronic ester based reversible and dynamic covalent cross-linking has been demonstrated to be an effective method for the preparation of self-healing gels.^[40,41] Boronic ester can hydrolyze to its constituent boronic acid and diol components at wet conditions while boronic acid and diol components can form boronic ester at dry conditions. Otherwise, most of boronic ester-based gels are responsive to different stimuli such as pH and temperature due to their inherent stimuli-sensitive properties, which is also decided by block polymers. Gels have exhibited potentials about self-healing properties under external chemical and physical stimuli. Here, a network was formed in the ionic/DCB gel *via* a dynamic covalent cross-linking reaction between 4-VPBA and di-hydroxyl groups attached to the imidazolium cations, as well as electrostatic interaction between sulfonate ion of AMPSLi and imidazolium cations. For the ionic gel, a network was formed through a one-step free radical co-polymerization of EVIMBr and AMPSLi, in which EVIMBr offers positive charge while the sulfonate ion of AMPSLi sup-



Scheme 1 Synthetic routes to ionic/DCB gel, ionic gel, and DCB gel investigated in this work

plies negative charge. Two chains interacted with each other through the electrostatic interaction. In the case of DCB gel, a network was also formed through free radical polymerization of neutral compounds, in which DCB of boronic ester were formed between 4-VPBA and HEMA.

The thermal transition properties of three gels were measured by differential scanning calorimetry (DSC) to explore their glass transition temperature (T_g), as shown in Fig. S4 (in ESI). The T_g value of DCB gel was 41.9 °C, indicating that it is difficult to be self-healed at room temperature, while the T_g values of ionic/DCB gel and ionic gel were determined to be -75.7 and -53.9 °C, respectively. Therefore, both ionic/DCB gel and ionic gel could perform self-healing to a certain extent. It should be noted that the added IL small molecules acted as a bridged linkage, which contributed to the formation of DCB and electrostatic interaction simultaneously. It can be deduced that ILs improved the chain mobility sufficient enough to trigger the self-healing behavior. Moreover, intermolecular diffusion of amorphous chains with the low T_g value further improved the healing ability of ionic/DCB gel. Thermogravimetric analyses (TGA) were also performed to test the thermal stability of ionic/DCB gels. As shown in Fig. S4(b) (in ESI), the weight of ionic/DCB gel was almost constant at 100 and 200 °C, indicating relatively high thermal stability.

To investigate the self-healing behavior of ionic/DCB gels, the gel samples were scratched. Figs. 1(a)–(d) show the healing process at 30 °C observed by optical microscopy. It can be seen that the scar was slightly healed after 3 h at 30 °C, and completely healed after 12 h, indicating good self-healing property. Fig. 1(e) shows the macroscopical healing test of the ionic/DCB gels. The ionic/DCB gel was cut into two pieces (one dyed red for clarity) and put together at 30 °C. The self-healed sample could withstand stretching to a large extent after contacting for 10 min. This result further confirmed the excellent self-healing behavior of ionic/DCB gels. In the case of ionic/DCB gels, the polymer chains were cross-linked by reversible DCB and electrostatic interaction. The incorporation of both two effects endowed the

polymer with the capability to self-heal autonomously.

The self-healing behavior of ionic/DCB and ionic gels was further investigated by tensile test. The original ionic/DCB gel showed the maximum stress of ~99.4 kPa at 30 °C (Fig. 2a). The maximum stress decreased to ~25.7 kPa after the cutting and 1 h self-healing, and then recovered back to ~40.1 and ~63.8 kPa after 3 and 6 h self-healing at 30 °C, respectively. On the other hand, the strain at break of the original ionic/DCB gel was ~570%, while decreased to ~180% and ~440% after 1 and 6 h self-healing at 30 °C. The self-healing efficiency (H) of ionic/DCB gel was about 77.4% at 30 °C, and could be increased to about 84.1% at 60 °C (Fig. 2b), probably due to the enhanced chain mobility of polymer backbone. Similar results were observed for ionic gels. The self-healing efficiency (H) of ionic gel was increased from about 37.9% to 82.5% as the temperature raised from 30 °C to 60 °C (Figs. 2c and 2d), respectively. Since the DCB gels were brittle and stiff at room temperature (T_g : 41.9 °C), the self-healing behavior of the DCB gels was tested at 80 °C (Fig. S5 in ESI). As can be seen, two cut pieces of gels (one dyed red for clarity) could be reconnected after re-contacting for 10 min. Fig. S6 (in ESI) shows the uniaxial tensile test of the ionic/DCB gel. The gel did not fracture even after being stretched about 6-fold of the initial dimension, indicating good stretchability. The dynamic rheological behavior of the ionic/DCB gel was also investigated. Fig. 2(e) shows the time dependence of storage modulus G' and loss modulus G'' of ionic/DCB gel at 30 °C. It can be seen that the values of G' were always higher than those of G'' , indicating the normal gel state. Fig. 2(f) exhibits the frequency sweep mode from 1 rad/s to 100 rad/s at 30 °C. Both G' and G'' of the ionic/DCB gel increased with the increase of frequency, which may be related to the relaxation of DCB between boronic ester and di-hydroxyl groups attached to the imidazolium cations.

To gain further insight into DCB and electrostatic interaction, density functional theory (DFT) calculations were carried out at the ω B97X-D/6-31G (d, p) level of the theory.^[42] Here, the ω B97X-D function was chosen due to its precise

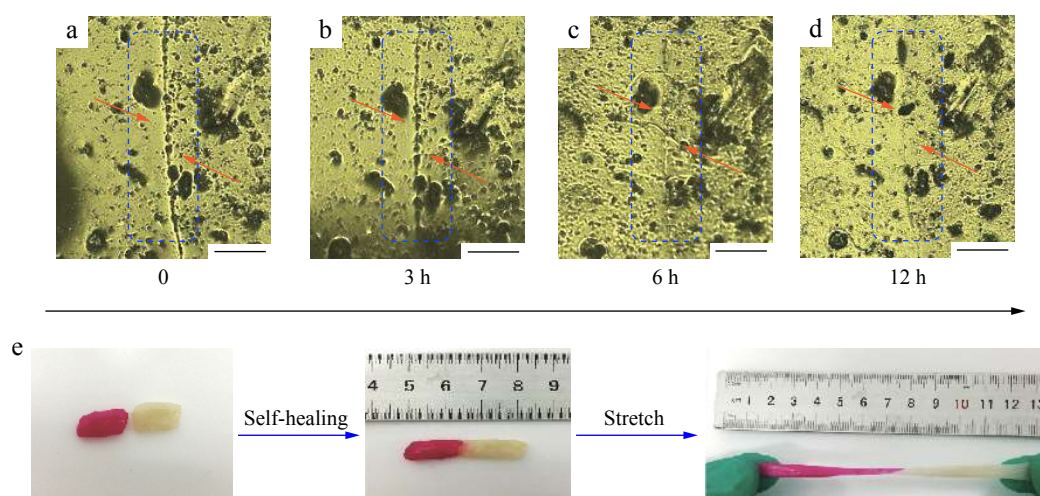


Fig. 1 (a–d) Optical microscopic images showing the healing for ionic/DCB gel at 30 °C as a function of time (Scale bar: 50 μm); (e) Photos showing the self-healing behavior of the dyed ionic/DCB gel

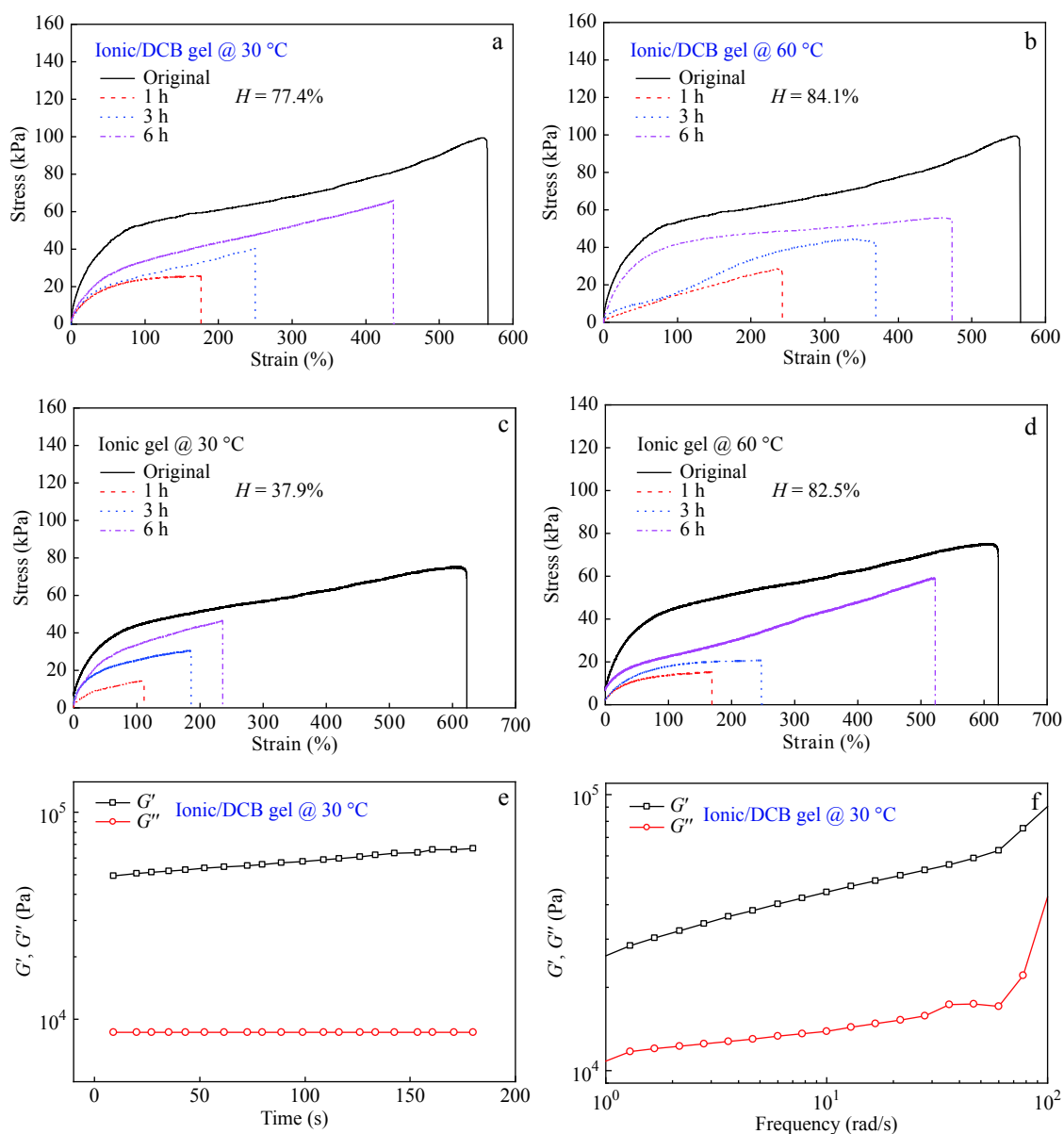


Fig. 2 Typical stress-strain curves of original and healed ionic/DCB gel and ionic gel samples for various healing times at 30 and 60 °C, respectively: ionic/DCB gel at (a) 30 °C and (b) 60 °C; ionic gel at (c) 30 °C and (d) 60 °C (H represents the self-healing efficiency of gels.); Dynamic rheological behaviors of ionic/DCB gel: (e) time dependence of storage modulus G' and loss modulus G'' at 30 °C and (f) frequency dependences of storage modulus G' and loss modulus G'' at 30 °C

description of thermochemistry for both ionic and neutral molecules. It is meaningful to calculate the forces between chain segments; therefore, the chain segments were used as the core for (DFT) calculations. Fig. 3 shows the DFT-optimized structure of three gels. Oligomers ($n = 2$) of three gels were employed to explore the interactions between boronic esters or imidazolium cation and sulfonate anion. Binding energy of about 65.42, 77.69, and 198.28 kJ/mol was obtained for ionic/DCB, ionic, and DCB gels, respectively. DCB gel had the highest binding energy between the intermolecular chains and the network became the most stable among three gels. Thus, it is not surprising that DCB gels were brittle and showed the lowest self-healing ability. The simulated results agree well with the experimental data ob-

tained.

To further investigate the practical applications of ionic/DCB gel in electronic devices, a quasi-solid-state lithium-sulfur battery (LSB) was assembled with cathode, anode, and a separator (ionic/DCB gel). As indicated in Fig. 4(a), the fast transportation of electropositive lithium ion could be achieved due to high ion conduction rate provided by our ionic/DCB gel. On the other hand, the ionic/DCB gel based separator could alleviate the shuttle effects (resulting from the dissociation and migration of electronegative polysulfides) by chemical sorption with the aid of sulfonate anions anchored on ionic/DCB gel backbones. The conductivity of the ionic/DCB gel was calculated to be about 0.59 S/m at room temperature by Nyquist plots, enabling its feasibility in

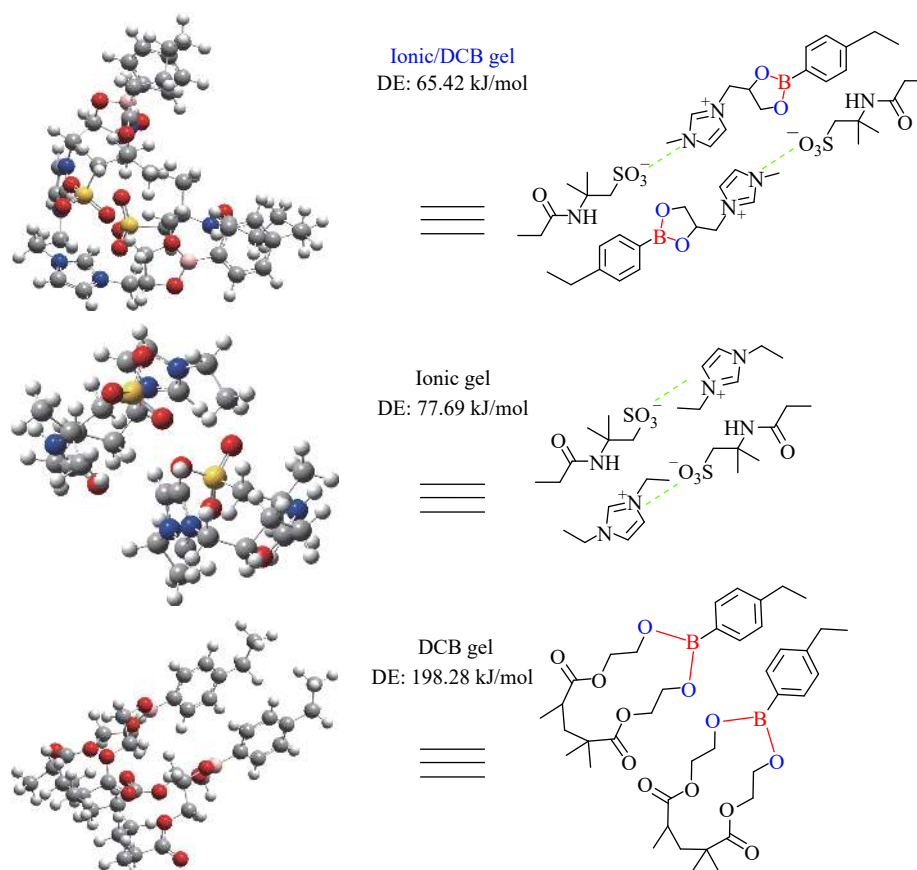


Fig. 3 DFT-optimized structure of ionic/DCB gel, ionic gel, and DCB gel. All DFT calculations were performed at the ω B97X-D/6-31G (d, p) level of theory.

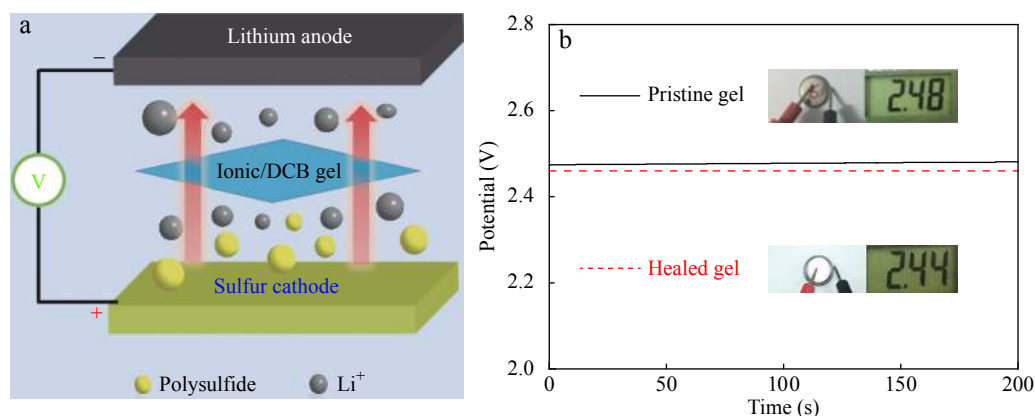


Fig. 4 (a) Schematic illustration of lithium-sulfur battery based on ionic/DCB gel; (b) Photo image and open circuit voltage of pristine and healed ionic/DCB gel based lithium-sulfur battery

LSB (Fig. S7 in ESI). It can be seen from Fig. 4(b) that the open circuit voltage of the LSB remained at 2.4 V steadily, indicating the successful assembly of the battery based on pristine and healed ionic/DCB gel separator. Fig. S8(a) (in ESI) shows the cyclic voltammetry (CV) curve of LSB with a scan rate of 0.1 mV/s. Obviously, three sharp peaks at 2.0 and 2.21 V correspond to the reduction potential as well as oxidation potential at 2.53 V of elemental sulfur. Fig. S8(b) (in ESI) shows the charge/discharge performances of LSB, suggesting that LSB possessed the relatively high specific capacity. Above results indicate that ionic/DCB gel separat-

or would be applied for lithium-sulfur applications.

CONCLUSIONS

In summary, a conductive and stretchable ionic/DCB gel with good self-healing ability was successfully prepared. The imidazolium type IL with di-hydroxyl group serving as the bridged linkage provided reversible DCB and electrostatic interaction with anions in the gel. We further demonstrated that the conductive ionic/DCB gel could be applied in lithium-sulfur battery because of the existence of sulfonate

anions which could alleviate the migration of electronegative polysulfide. We expect that the promising approach of making use of reversible DCB and electrostatic interaction simultaneously will be an efficient tool to prepare self-healing ionic gels, and offer a new gel platform for developing of smart self-healing devices and biomedical materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-019-2325-x>.

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