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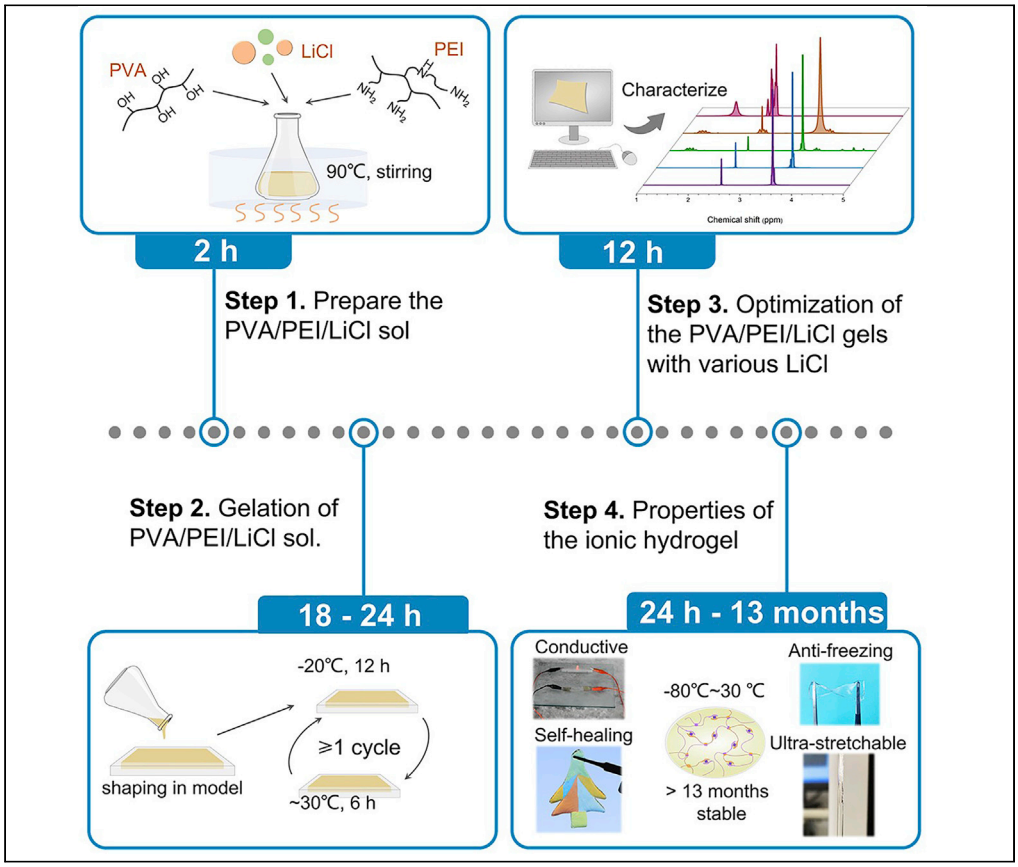
Protocol to fabricate ionic hydrogel with ultra-stretchable and fast self-healing ability in cryogenic environments



Self-healing materials exhibit irreplaceable advantages in artificial electronics given their ability to repair from accidental damage, but the self-healing ability is temperature sensitive, limiting their applications in cryogenic environments. Here, we describe steps to fabricate a versatile ionic hydrogel with fast self-healing ability, ultra-stretchability, and stable conductivity, under the temperature ranging from −80°C to 30°C. We also detail steps for characterizing the polymer structure and interactions of the ionic hydrogel, as well as the mechanical, electrical, and self-healing properties.

Publisher's note: Undertaking any experimental protocol requires adherence to local institutional guidelines for laboratory safety and ethics.

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Highlights

Fabrication strategy to design the ionic hydrogel with multifunction

Characterize the structure and interactions of the ionic hydrogel

Explore the anti-freezing ability of the ionic hydrogel under cryogenic temperatures

Study the ultra-stretchability, conductivity, and self-healing ability of ionic hydrogel

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Protocol to fabricate ionic hydrogel with ultra-stretchable and fast self-healing ability in cryogenic environments

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SUMMARY

Self-healing materials exhibit irreplaceable advantages in artificial electronics given their ability to repair from accidental damage, but the self-healing ability is temperature sensitive, limiting their applications in cryogenic environments. Here, we describe steps to fabricate a versatile ionic hydrogel with fast self-healing ability, ultra-stretchability, and stable conductivity, under the temperature ranging from −80°C to 30°C. We also detail steps for characterizing the polymer structure and interactions of the ionic hydrogel, as well as the mechanical, electrical, and self-healing properties.

For complete details on the use and execution of this protocol, please refer to Wang et al. (2022).[1]

BEFORE YOU BEGIN

Biological systems, such as human skin, can self-heal from wounds, allowing it to restore mechanical and biological functions, which inspired us to design artificial electronics.[2,3] Numerous intrinsic self-healing materials have been designed based on physical interdiffusion,[4] dynamic interactions,[5] and Van der Waals forces.[4] They were successfully integrated into functional devices,[6] such as electronic accessories,[7] bioelectronic devices,[8,9] and energy harvesting/storage devices.[10] However, despite those promises, few self-healing materials maintain functions at sub-zero temperatures, which largely limits their applications in cryogenic environments. The temperature-sensitive intrinsic self-healing process is based on two important features. Including the diffusion of polymer chains and the reformation of broken dynamic bonds. At sub-zero temperatures, the two processes become slow or even prohibited.

In our previous study, we designed fast self-healing ionic hydrogels for cryogenic environments, through the following strategies: (i) increasing the mobility of polymer segments and (ii) increasing active dynamic interactions. Further, the optimized ionic hydrogels achieved over 70 times ultra-stretchability, stable conductivity, and over 13 months of properties stability. With these advantages, this multifunctional ionic hydrogel exhibited its broad application potential in new-generation self-healing artificial electronics. Here, this protocol directly and in detail describes the designing and fabricating process of polyvinyl alcohol (PVA)/Polyethyleneimine (PEI)/lithium chloride (LiCl) based ternary ionic hydrogels. The properties optimization strategy is recorded and discussed.

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Polyethyleneimine (PEI, anhydrous, M.W. 600, 99.8%)	Aladdin Biochemical Technology Co., Ltd.	CAS: 9002-98-6
Lithium chloride (LiCl, anhydrous, AR)	Maclean Biochemical Technology Co., Ltd.	CAS: 7447-41-8
Titanium foil (99.9%)	Sennuo Material Technology Co., Ltd.	Ti42314
Deuterated polydimethyl sulfoxide (DMSO, D.99.8% +0.03%TMS)	Shanghai Acmec Biochemical Co., Ltd	CAS: 2206-27-1
Dry ice	Huali De Technology Co., Ltd.	1452874
Other		
20 mL vial	Huali De Technology Co., Ltd.	DB233
Magneton (C25)	Ruixin Biochemical Technology Co., Ltd.	RX04-103-5CX
Collecting heat magnetic stirrer water bath (220 V/ 50 Hz)	Guangzhou Zhiyan Instrument Co., Ltd.	DF-101S
NMR tube (5 mm)	Wilmad	wg-1000-7
Glass based mold	Lab-made	N/A
−20°C freezer	Haier	BCD-272WDPD
−80°C refrigerator	Thermo ScientificTM	Forma 900 series
Balance	Sail Huachuang Technology Co., Ltd.	QF203P
Magnetic stirring table	Lige Technology Co., Ltd.	LG-DL-63S
X-ray diffraction (XRD)	Malvern PANalytical	X'Pert3 Powder
X-ray photoelectron spectroscopy (XPS)	ULVAC-PHI, Inc.	PHI 5000 Versa Probe III
Proton nuclear magnetic resonance (^{1}H NMR)	Swiss Bruker	AVANCE III 600 MHz
Dynamic thermomechanical analyzer (DMA)	TA Instruments	Q800
Optical microscope	Nikon	Nikon ECLIPSE 3 × 2 STAGE
Force and torque measurement	Mark-10	ESM 303
Electrochemical workstation	Shanghai Chenhua Instrument	CHI 660E
Temperature control station	Linkam	LTSE420

Note: To avoid the redox reaction between the electrode and the electrolyte during the electrochemical impedance test, we use two titanium foils as the contact electrodes with the ionic hydrogel. At the same time, appropriate pressure was applied to ensure close contact between the ionic hydrogel and electrodes.

Optional: Instead of Ti electrodes, electrodes of flexible substrate sputtered with gold or silver are available, too.

STEP-BY-STEP METHOD DETAILS

PVA/PEI/LiCl ionic sol synthesis with a one-pot method

Timing: 2–3 h

Before this step, the following tools should be ready: a cleaned beaker, measuring cylinder, cleaned vial with stirring bar, stirrers, and weighing paper. Set the water bath at 90°C and preheat for 30 min.

1. Prepare the mixed precursor of PVA, PEI, and LiCl.
   a. Weigh 9.0 mL DI water with a measuring cylinder. Then, store the water in a 20 mL vial.
   b. Weigh 4.0 g LiCl powder with a microbalance.

Table 1. The ionic hydrogel with various LiCl content

LiCl content	LiCl (g)	PVA (g)	PEI (g)	Water (mL)
0%	0.0	2.0	1.0	9.0
4%	0.5	2.0	1.0	9.0
14%	2.0	2.0	1.0	9.0
20%	3.0	2.0	1.0	9.0
25%	4.0	2.0	1.0	9.0

c. Pour the LiCl powder into the vial.
d. Stir the mixture with a magnetic stirrer plate to help the LiCl dissolve quickly to get the LiCl solution.

Note: LiCl is corrosive to mucous membranes, operators should try to avoid LiCl contacting with eyes. Furtherly, LiCl powder is hygroscopic and should be stored in an inert atmosphere. To avoid a large amount of water absorption by LiCl, the operation speed should be as fast as possible during the weighing process.

e. Weight 1.0 g PEI liquid with a microbalance into the LiCl solution.
f. Stir the mixture with a stirring bar until the PEI is completely dissolved.
g. Weight 2.0 g PVA powder with a microbalance.
h. Pour the PVA powder into the LiCl/PEI solution and mix them with a stirring bar for 5 min.

2. Put the vial into the 90°C water bath.
3. Set the stirring speed to 150 rpm and the heating time to 2 h.
4. The PVA/PEI/LiCl sol becomes viscous and transparent after the water bath process.

⚠ CRITICAL: The moisture will evaporate very quickly at 90°C. The operator should observe the water level during the experiment in case the water bath dries out. When the operator moves this vial, please take care because the vital is very hot.

Optional: Instead of the water bath, oil bath and constant temperature oven, a reaction kettle can be used to create a constant temperature environment.

Note: The contents of LiCl have significant effects on the electrical conductivity, frost resistance, self-healing properties, and stretchability of the ionic hydrogel. Samples with different LiCl content were prepared, the details are shown in Table 1.

The transition of PVA/PEI/LiCl ionic hydrogel from sol

Timing: 18–24 h

Before this step, the cleaned glass mold should be ready.

5. Open the vial and pour the sol into a glass mold.

Note: The sol is very viscous with a very slow flow rate. Thus, this step will take more than ten minutes. It is wise not to use a stir bar to aid in gel transfer because air bubbles are easily introduced.

6. Cover the groove of the mold with another piece of glass.
7. Squeeze them firmly so that the coverslip is in close contact with the hydrogel.
8. Secure the two pieces of glass with four dovetail clips.
9. Store them in a −20°C refrigerator for over 12 h.

10. After that, take out the samples and leave them at 27°C for over 6 h.

Characterizations of the PVA/PEI/LiCl ionic hydrogel

Timing: about 12 h

To better understand the structure and internal interactions of the ternary ionic hydrogel, as well as the effect of LiCl among the system, X-ray diffraction (XRD), ^{1}H NMR and X-ray photoelectron spectroscopy (XPS) are performed.

11. Cut the prepared ionic hydrogel samples with various LiCl content all in the size of 10 × 10 × 1 mm^3 for XRD analysis.
12. Prepare ionic hydrogel samples for XPS analysis.
    a. Prepare the ionic hydrogel samples with 0% and 4% LiCl content all in the size of 10 × 10 × 1 mm^3.
    b. Dehydrate all samples in a freeze dryer for 3 days to obtain samples that are dry but contained the original structure.
13. Prepare ionic hydrogel samples for ^{1}H NMR analysis.
    a. Prepare the ionic hydrogel samples with various LiCl content, keep all samples weight are 1.0 g.
    b. Dissolve samples in the 0.55 mL deuterated DMSO with heating and stirring.

Note: The dissolution process is slow and will take about 2–3 hours. Considering there is a large water content in the ionic hydrogel. The high intensity of the water peak may influence our analysis results. The ^{1}H NMR spectrum of pure water was performed for reference (Figure 1E).

Anti-freezing measurement

Timing: 3–4 weeks

This step aims to explore the effect of LiCl content on the anti-freezing properties of ionic hydrogels.

14. Prepare all ionic hydrogels with 0%, 4%, 14%, 20% and 25% LiCl in size of 30 × 10 × 2 mm^3.
15. Store all samples in a −80°C refrigerator for 3–4 weeks.
16. Take out samples one by one, observing:
    a. Frozen or not.
    b. Transparency.
    c. Flexibility and stretchability.
17. Record the status of all samples by taking photographs.

⚠ CRITICAL: −80°C can cause frostbite to human tissue, do not stay in this environment for a long time and pay attention to wearing protective gloves.

Note: Considering the large temperature difference between 27°C and −80°C, a rapid heat exchange occurs after taking samples out of the freezer, which changes the gel's frozen state. Therefore, the test process should be undergone one by one at a fast speed. Furtherly, dry ice can be used to create a local low-temperature environment.

Mechanical measurement at around 27°C

Timing: ~6 h

This step aims to explore the effect of LiCl content on the stretchability, strength, and fatigue resistance of ionic hydrogels. Before this step, prepare all samples in size of 10 × 10 × 1 mm^3.

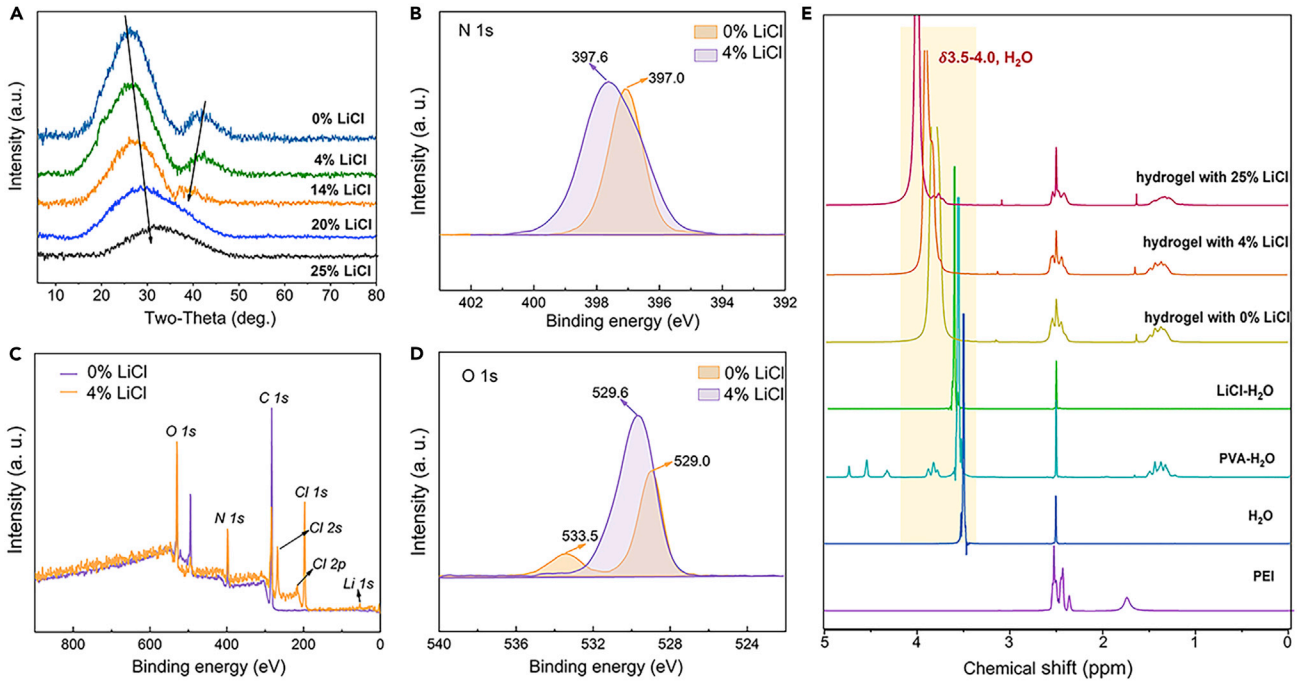

Figure 1. Characterizations of the ionic hydrogels with various LiCl content

(A) XRD spectrum of ionic hydrogels with various LiCl content.

(B–D) XPS analysis of ionic hydrogels with 0% and 4% LiCl.

(E) ^{1}H NMR spectra (*d6*-DMSO) of PEI, H_2O, PVA-H_2O, LiCl-H_2O, ionic hydrogels with 0%, 4% and 25% LiCl.

Reproduced with permission (Wang et al.).[1]

18. Accurately measure the width and thickness of each sample with a vernier caliper.
19. Record all dates.

Note: Because the ionic hydrogel is soft and stretchable, its actual size will be affected by pulling during transfer.

20. Clamp the sample between the two grips, like in Figure 2.
21. Test and record the distance between two grips.

Note: The strain (ε) and stress (δ) can be calculated according to the equation below and the size of the sample.

$$\varepsilon = \frac{L - L_0}{L_0}$$

$$\delta = \frac{F \times L_0}{A \times \Delta L}$$

Where, ΔL is the length change of ionic hydrogel after stretching; L_0 is the original length between two grips; F is the force tested by ESM301/Mark-10 system at the breaking point; A is the cross-sectional area of the original ionic hydrogel between two grips.

22. Set tensile loading speed as 30 mm/min.

Note: The tensile loading speed has a great influence on the calculated strain and strength of soft materials. The loading speed can be set according to requirements.

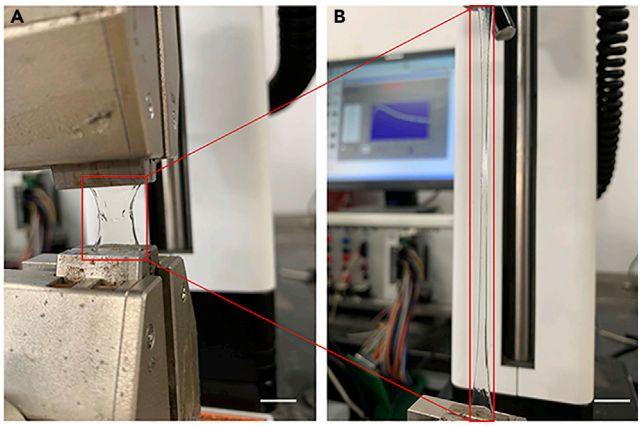

Figure 2. The stretchability was tested with ESM301/Mark-10 system
(A) The sample was clamped between two grips. The length of the sample between two grips is about 10 mm.
(B) The sample after stretching. Scale bar in (A) and (B) are 10 mm.

23. Start the test program of ESM301/Mark-10.
24. Stop the test program of ESM301/Mark-10 after the sample is broken due to over-stretching.
25. Save the test data from ESM301/Mark-10.
26. Remove the tested sample from ESM301/Mark-10.

Electrochemical measurement

Timing: ~3 h

This step aims to explore the effect of LiCl content on the conductivity of ionic hydrogels through the electrochemical impedance (EIS). Before this step, the temperature control station should be ready and linked with the electrochemical workstation (Shown in Figure 3).

27. Prepare the samples in the required size and record their dimension parameters.
28. Put the ionic hydrogel sample on the temperature control platform.
29. Insert two probes of the temperature control station into the ionic hydrogel at a fixed distance.
30. Set the temperature of the platform to 30°C and keep this temperature for a while.
31. Set up the electrochemical workstation's test parameters for EIS.
32. Start the test.
33. Save EIS dates.
34. Test three times each sample.

Optional: Set the temperature as 0°C, −20°C, −50°C and −80°C for testing the conductivity under cryogenic environments.

⚠ CRITICAL: During the test, the cold platform may cause frostbite to human tissue, please pay attention to wearing protective gloves.

Self-healing measurement

Timing: 5–12 h

This step aims to explore the self-healing performance of ionic hydrogel under temperatures ranging from −80°C to 30°C. There are three strategies to represent self-healing performance:

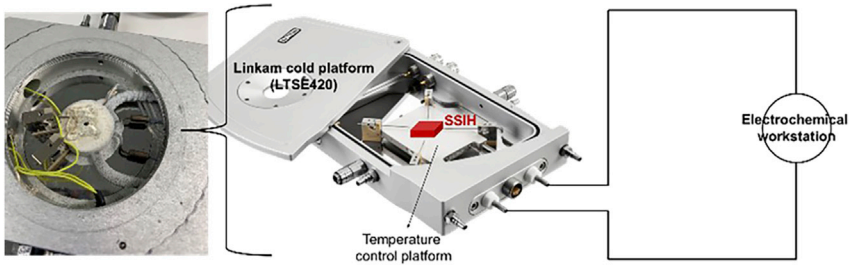

Figure 3. The electrochemical performance of ionic hydrogels tested with LTSE420/CHI 660E

(i) by testing tensile strain-stress curve; (ii) by testing the resistance; and (iii) by observing the healed incision with light microscopy.

35. Prepare ionic hydrogels in size of 10 × 30 × 1 mm^3.
36. Store the ionic hydrogel samples in a −80°C refrigerator for 2 h.
37. Take out the ionic hydrogel samples.
38. Cut one sample in half with a scissor, gently put the incisions together, and put them back to the −80°C refrigerator.
39. Take out the healed ionic hydrogel after 30 min of healing.

Optional: The test of the self-healing ability of the ionic hydrogel under −50°C, −20°C, 0°C and 30°C follow the same procedure.

Optional: The self-healing time could be designed according to requirements.

40. Analyze self-healing efficiency by a tensile stress-strain curve (as shown in Figure 4).
    a. Prescribe the healed sample between two grips of the ESM301/Mark-10 system.
    b. Test its tensile stress-strain curve at a speed of 30 mm/min.
    c. Save test dates after the healed samples were broken.
    d. Analyze test results and calculate the max stretchability.
    e. Calculate the self-healing efficiency according to the ratio of the stretchability of healed sample and the stretchability of the original sample in the same condition.
41. Analyze self-healing efficiency by conductivity.
    a. Link the healed sample with an electrochemical workstation.
    b. Test its EIS performance.
    c. Save the test date.
    d. Analyze test results and calculate equivalent resistance (ER) of samples.
    e. Calculate the self-healing efficiency according to the ratio of the ER of healed sample and the ER of the original sample in the same condition.
42. Analyze self-healing performance by observing the healed incision with microscopy (as shown in Figure 5).
    a. Place the healed sample on the stage of microscopy.
    b. Adjust the parameters so that the healed incision can be displayed in the field of vision.
    c. Photograph the healed incision.
    d. Compare the healed incisions at different healing times and analyze the self-healing efficiency.

Optional: The self-healing efficiency also can be calculated from the dissipated energy and Young's modulus at the breaking point.

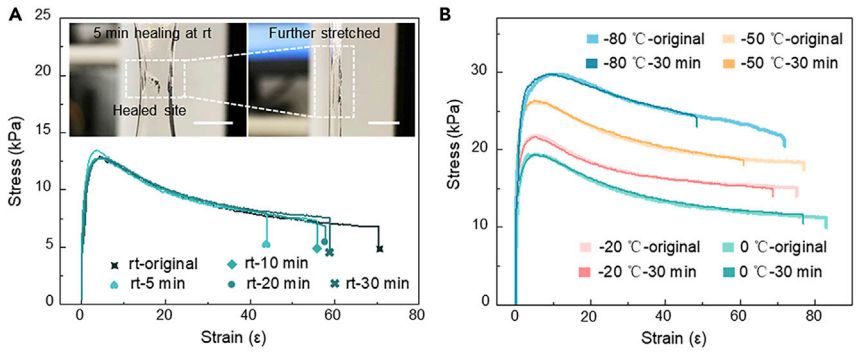

Figure 4. The tensile stress–strain curves of the ionic hydrogel at the original state and after 30 min healing in various temperatures

(A) The tensile tress–strain curves of the ionic hydrogel at the original state and different healing times at 27°C. The insets show notch of the ionic hydrogel at stretched states after 5 min healing. Scale bar: 1 cm.

(B) The tensile stress–strain curves of the ionic hydrogel at the original state and after 30 min healing in cryogenic temperatures. Loading rate: 30 mm/min. Reproduced with permission (Wang et al.).[1]

Note: As the healing temperature increased, the time required to achieve the same healing effect was shorter. The healing effect will be better as the healing time increases. For most samples, it is difficult to achieve 100% healing efficiency, because when the incision is created, the morphology of the sample at the incision changes, resulting in the two halves can't be perfectly aligned.

EXPECTED OUTCOMES

In this protocol, the main experimental variable affecting the performance of the ionic hydrogel is the LiCl content. With the increase of LiCl content, the frost resistance enhances, the electrical conductivity increase, the self-healing ability improve, and the maximum stretchability rise. At the same time, the mechanical modulus decreases. The ionic hydrogel with 25% LiCl shows optimal performance in realizing over 70 times stretchability, stable conductivity, fast self-healing, and over 13 months of properties stability, under temperatures ranging from −80°C to 30°C. The self-healing efficiency can be improved by increasing the environment temperature and extending healing time. With the above superior properties, the versatile ionic hydrogels realize their broad application in the new generation of artificial intelligent electronics.

QUANTIFICATION AND STATISTICAL ANALYSIS

XRD is performed with 2θ ranging from 5° to 80°, where Cu K_α radiation (λ = 1.5406 Å) is operated at 40 kV and 40 mA.

XPS spectra are recorded by PHI 5000 Versa Probe III with aluminum K_α source (1848.6 eV) and a collimator at 15 kV and 50 W. The high-resolution survey of nitrogen and oxygen is performed with pass energy = 69 eV.

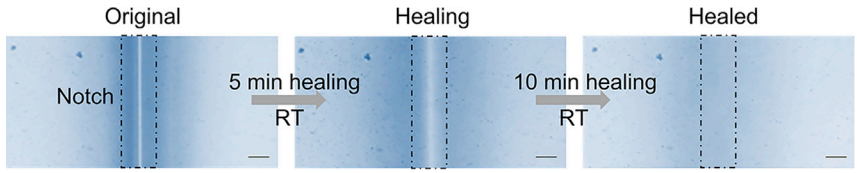

Figure 5. The self-healing process of the damaged ionic hydrogel was observed through the optical microscope

Scale bar: 1 mm. Reproduced with permission (Wang et al.).[1]

^{1}H NMR spectrum is recorded on a Bruker AVANCE III 700 MHz spectrometer with deuterated DMSO as solvent at 27°C.

The EIS curves are performed with frequency from 1 MHz to 0.1 Hz, with the AC potential amplitude of 10 mV.

LIMITATIONS

In this protocol, the most important point is the ternary system should be built with two complementary long and short polymers and one kind of colligative inorganic salt. These two polymers contain a large number of functional groups with opposite polarities. The inorganic salt with high hydration energy plays a role in reducing the degree of crystallinity and providing conductive ions. Therefore, it's not applicable to all neutral polymer systems, polymer systems with the same polarity, and non-collinear inorganic salts.

TROUBLESHOOTING

Problem 1

The order in which the PVA, PEI, and LiCl dissolve in water is important (step 1. PVA/PEI/LiCl ionic sol synthesis with a one-pot method).

Potential solution

LiCl and PEI are soluble at 27°C, they can be dissolved in water first, then add PVA, and stir evenly. Then, put the mixture in the water bath.

Problem 2

In the ^{1}H NMR, the peak from a large amount of water in the ionic hydrogel masks other signals (step 13. Prepare ionic hydrogel samples for ^{1}H NMR analysis).

Potential solution

Record ^{1}HNR spectrum of pure water and LiCl aqueous solution, PEI aqueous solution and PVA hydrogel as a reference.

Problem 3

It's not easy to dissolve the ionic hydrogel based on PVA/PEI/LiCl into deuterated DMSO (step 13. Prepare ionic hydrogel samples for ^{1}H NMR analysis).

Potential solution

It can be dissolved by heating, stirring and portending dissolving time.

Problem 4

The striction of the soft materials during stretching causes the dimensional parameters of the tested sample to change in real-time, which leads to inaccurate calculations of strength (modules).

Potential solution

Under certain circumstances, the equation can be corrected as:

$$\delta^{*} = \frac{F \times L_0}{\varepsilon \times A \times \Delta L}$$

Where, δ^{*} is corrected stress, ε is strain.

Problem 5

When the tensile deformation is more than 70 times, the deformation length may exceed the test range of the ESM301/Mark-10 (steps 18–26. Mechanical measurement of the ionic hydrogel).

Potential solution

When the tensile distance reaches the max test distance of ESM301/Mark-10, the tested sample is not pulled off. The tensile test can be carried out again by cutting a length in the middle of the tested sample. Then the total tensile deformation should be calculated as:

$$\varepsilon = \boldsymbol{\varepsilon}_1 \times \boldsymbol{\varepsilon}_2 \cdots \times \boldsymbol{\varepsilon}_i$$

Where, $\boldsymbol{\varepsilon}_1$ is the tensile ratio of the first stage, $\boldsymbol{\varepsilon}_2$ is the tensile ratio of the second stage, $\boldsymbol{\varepsilon}_i$ is the tensile ratio of the i^{th} stage.

Problem 6

How to create a local hypothermia environment at room temperature for the test? (steps 27–34. Electrical measurement at sub-zero temperatures; steps 40–41. Self-healing measurement at sub-zero temperatures).

Potential solution

The temperature control platform (temperature control station), dry ice, and liquid nitrogen can be used to create the local cryogenic environments.

Problem 7

It's not easy to focus on the healed incision under an optical microscope since the healed incision maybe not be on a horizontal plane (step 42. Analyze self-healing performance by observing the healed incision by microscopy).

Potential solution

Place a piece of plasticine under the healed sample. Adjust the level of the tested sample by changing the shape of the plasticine.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Zhou Li (zli@binn.cas.cn).

Materials availability

This study did not generate any new unique reagents.

Data and code availability

Data and code would be made available upon request.

ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS

Z.L. conceived and supervised the project. C.W. and Y.L. designed and performed all the experiments and data analysis.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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