

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

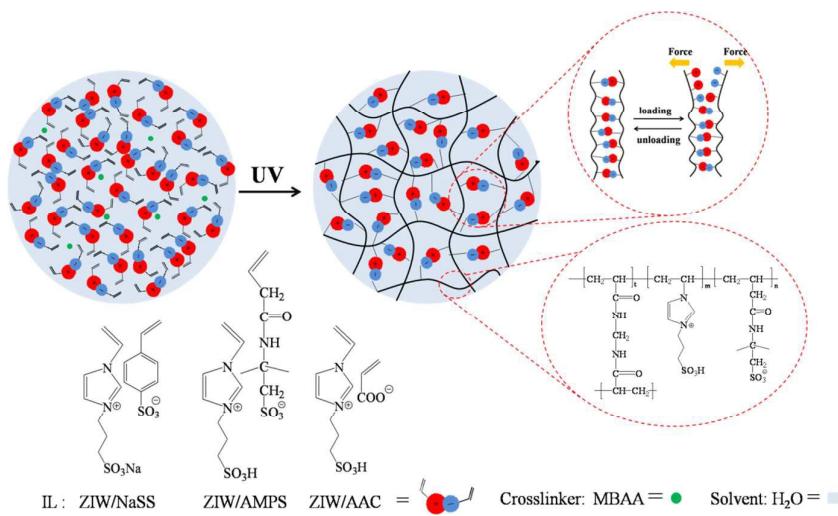
Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

The Table of Contents

Flexible poly(ionic liquid)s hydrogels with polymerized anions and cations exhibit superior electrochemical properties, which can remain stable under different deformations.





Poly(Ionic Liquid)s Hydrogels Exhibiting Superior Mechanical and Electrochemical Properties as Flexible Electrolytes

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/Tao Zhou^a, Xinpei Gao^a, Bin Dong^b, Na Sun^a, Liqiang Zheng^{*a}

Recently, flexible electrolytes have aroused tremendous interests due to their wide applications in flexible electronic devices, such as wearable electronics, roll-up displays, smart mobile devices and implantable biosensors. Herein, novel ionic liquids, whose cations and anions both can be polymerized, are used to construct flexible poly(ionic liquid)s hydrogel electrolytes by one-step synthesis. Originating from the ionic interactions inside the ionic liquids, these hydrogels combine strong and weak crosslinks after polymerized, which makes these hydrogels tough, stretchable, flexible and self-recovery. Their superior mechanical properties have been certified by mechanical tests. Moreover, these poly(ionic liquid)s hydrogels show extremely high ionic conductivities over 1 S m^{-1} at room temperature and low activation energy. Notably, their electrochemical behaviors can remain stable under different bending angles and successive bending, folding, compressing and twisting. As flexible electrolytes, these poly(ionic liquid)s hydrogels give the possibility to be used in fuel cells or supercapacitors, thus, promoting the developments of the flexible electronic devices.

Introduction

Recently, flexible electronic devices, such as wearable electronics, smart mobile devices, roll-up displays and implantable biosensors, have attracted tremendous attentions due to their wide application prospects and superior characteristics compared with conventional electronic devices, namely, portable, lightweight, bendable, wearable and even implantable.¹⁻⁵ And the increasing demand of flexible electronic devices has stimulated the progress in the corresponding flexible energy storage and conversion devices with high performance, e.g. supercapacitors (SCs),^{6,7} lithium-ion batteries (LIBs),⁸⁻¹⁰ solar cells,¹¹⁻¹³ and fuel cells.¹⁴⁻¹⁷ For applications in practice, each component of the flexible energy storage and conversion devices must be mechanically stable and flexible. Moreover, these components should also have superior electrochemical properties, like high conductivities and electrochemical stabilities.¹⁸⁻²⁰ In order to meet these requirements, significant efforts have been made to explore suitable and effective materials. In spite of the exciting progress made to date, the challenges for manufacturing ideal flexible electronic devices are still huge, as they are still in the early stage of development.²¹

Currently, ionic liquids have been widely used in various fields, due to their unique and advantageous properties, that is, low volatility, non-flammability, high thermal stability, wide electric windows, high ionic conductivity.²²⁻²⁵ For instance, flexible supercapacitors based on ionic liquids have been successfully fabricated with very high specific capacitance of 244 F g^{-1} at room temperature.²⁶ However, leakage problems caused by ionic liquids may limit their applications in practical use.^{27,28} As a sub-discipline of ionic liquids, poly(ionic liquid)s have attractive mechanical characteristics of polymers, while retaining the superior physicochemical properties of ionic liquids.^{29,30} This special feature can help to overcome the key leakage and poor mechanical limitations of ionic liquids. Yan et al. prepared many excellent functional materials based on poly(ionic liquid)s, which have shown superior performances in electronic devices, like dye-sensitized solar cells (DSSCs).^{17,31-33} However, it should be noted that the incorporations of poly(ionic liquid)s into functional devices commonly require their shaping into processable materials, such as thin films and gels.³⁴ The latter composes a sought-after category of materials in future electronic devices, because of their high ionic conductivities, which are comparable to liquid electrolytes.^{35,36} To date, most of these poly(ionic liquid)s gels show poor mechanical properties, which definitely cannot be used in flexible electronic devices. Therefore, developing poly(ionic liquid)s gel electrolytes, which have simultaneously high ionic conductivity, good mechanical property and electrochemical stability, is desirable and very challenging.

Recently, tremendous progresses developing tough gels have been made, which display board application perspective, such as biomaterials, soft robotics, smart actuators, and sensors.^{37,38}

^a Key laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, P. R. China. E-mail address: lqzheng@sdu.edu.cn

^b Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023,

† Electronic Supplementary Information (ESI) available. SEM and DSC of poly(ionic liquid)s hydrogels; pictures of poly(ZIW/AMPS)s hydrogels under deformations See DOI: 10.1039/b000000x/

It is found that the combination of strong and weak crosslinks can promote gels' mechanical properties.^{39,40} For instance, a novel hydrogel by combining both covalent crosslinking and ion pairing of Fe³⁺-acrylic acid coordination has been prepared by Zhou et al. with ultrahigh tensile strength (≈ 6 MPa), large elongation (>7 times), ultrahigh toughness (≈ 27 MJ m⁻³) and good self-recovery property.⁴¹ Gong et al. demonstrated that polyelectrolyte hydrogels containing ionic bonds can possess superior mechanical characteristic.^{42,43} As we know, ionic liquids consist of organic cations and anions, which are connected by ionic bonds.²⁴ Based on previous works, gels based on poly(ionic liquids), whose cations and anions are polymerized, should display superior mechanical property as these poly(ionic liquids) gels will combine strong crosslinks (covalent crosslink) and weak crosslinks stemming from the ionic bonds within ionic liquids. Furthermore, these poly(ionic liquids) gels can maintain many characteristics of ionic liquids, like electrochemical properties, and thus exhibit broad application perspectives in flexible electronic devices.

In this work, a novel ionic liquid, 3-(1-vinyl-3-imidazolio)propanesulfonate/2-acrylamido-2-methylpropane sulphonic acid (ZIW/AMPS), is managed to prepare flexible poly(ionic liquid)s hydrogel electrolytes. As both the cations and anions of the novel ionic liquid contain carbon-carbon double bonds, these poly(ionic liquid)s hydrogels combine both strong and weak crosslinks after polymerized. The combination makes these hydrogel electrolytes tough, flexible and self-recovery, which has been certified by mechanical measurements. Moreover, these poly(ionic liquid)s hydrogel electrolytes exhibit extremely high conductivities over 1 S m⁻¹ at room temperature and low activation energy. Notably, their electrochemical behaviors could remain stable under different bending angles and successive bending, folding, compressing and twisting. As flexible electrolytes, these poly(ionic liquid)s hydrogels will promote the developments of the next-generation flexible electronic devices.

Experimental

Materials

The compounds 1-vinylimidazole, 1, 3-propanesultone, sodium p-styrenesulphonate (NaSS), 2-acrylamido-2-methylpropanesulphonic acid (AMPS), acrylic acid (AAC), crosslinker (MBAA) N,N'-methylenebis(2-propanamide), and the photoinitiator 1173 2-hydroxy-2-methylpropiophenone were acquired from J&K Scientific Co. Ltd. All the reagents were used without further purification. Deionized water was used through the experiments.

Synthesis of Zwitterions 3-(1-Vinyl-3-imidazolio)propanesulfonate (ZIW)

The compound 1-Vinylimidazole (6.3 g, 0.067 mol) was dissolved in 80 mL of acetone. Then, an equimolar amount of 1, 3-propanesultone (8.2g, 0.067 mol) in acetone (40 mL) was slowly added to the solution at 0 °C under a nitrogen atmosphere. The reaction mixture was then stirred for 5 days at room temperature.

After the reaction, the solution was filtered and the zwitterionic salt (ZIW) was twice purified with acetone. The ZIW was dried under a vacuum at room temperature and a white powder was obtained. The purity of the product was ascertained by the 1H NMR (300 MHz) in D₂O. δ (relative to TMS): 8.975 (1H, s), 7.668 (1H, d), 7.506 (1H, d), 6.984 (1H, q), 5.656 (1H, d), 5.290 (1H, d), 4.297 (2H, t), 2.832(2H, t), 2.230 (2H, m).

Synthesis of Poly(ZIW/AMPS)s Hydrogels

Poly(ZIW/AMPS)s precursor solutions containing prescribed masses of equal molar ZIW and AMPS were prepared in water. And then the crosslinker MBAA and photo-initiator 1173 (0.5 mol% in a concentration relative to the total ionic liquids concentration) were added to the above solution. After irradiating with 365 nm ultraviolet light for 1 h, the poly(ZIW+AMPS)s hydrogels were prepared. Other poly(ionic liquid)s hydrogels were prepared via the same process.

Fourier Transform Infrared Spectra

FT-IR spectra of the poly(ZIW+AMPS)s hydrogels after removing H₂O were taken in a KBr disc on a Nicolet/Nexus-670 FT-IR spectrometer in the range of 4000–450 cm⁻¹.

Thermal properties

DSC measurements were carried out on a PerkinElmer DSC 8500 under a nitrogen atmosphere. The sample was tightly sealed in aluminum pans and heated from 0 °C to 200 °C under a nitrogen atmosphere at a flow rate of 20 mL/min. The scan rate of DSC run is 10 °C/min.

Scanning Electron Microscope Micrographs

A FEI Nova Nano SEM 600 scanning electron microscope was used to obtain morphology micrographs of the hydrogels at ambient temperature and low vacuum. The hydrogels, after removing H₂O, was converted to xerogel by freeze-drying under vacuum. The xerogel was mounted on an aluminum stub and coated to 100-150 Å thick with Au by sputtering.

Mechanical Measurements

The compressive tests were performed with a commercial test machine (Tensile Tester AG-2000A, Shimadzu). The gels were cut into a disc shape and were sandwiched between the two plates. The silicone oil was coated the plates to reduce the friction between the gels and the plates during compressive experiments. The compressive rate was 5 mm min⁻¹ through the experiments. The Young's modulus was calculated from the slope of the stress-strain curves at small strain (within 10%).

Conductivity Measurements

The samples were measured in blocking-type cells where the poly(ZIW+AMPS)s hydrogels electrolytes were sandwiched between two stainless steel electrodes with a silica gel spacer and a

square hole.⁴⁴ The impedance measurements were taken in the temperature range of 30 °C ~ 80 °C over a frequency from 100 kHz to 10 mHz. The samples were thermally equilibrated at each temperature for 10 minutes before measurements. The bulk resistance of the poly(ionic liquid)s hydrogels electrolyte, R , can be calculated from the fitting procedure, and correspondingly the conductivity of the poly(ZIW/AMPS)s hydrogel electrolyte is estimated according to the following equation:

$$\sigma = l/(AR)$$

where l is the thickness of the electrolyte and A is the electrode area.

Results and Discussion

The synthetic process of poly(ZIW/AMPS)s hydrogels and structures of the used ionic liquids are illustrated in Fig. 1. In brief, precursor solutions were obtained by dissolving the crosslinker MBAA and equal molar of ZIW and AMPS in H₂O. Due to the strong dipole moments, the zwitterions can solvate various ionic salts.^{45,46} That is to say, the zwitterions (ZIW) are prone to combine with the ionic salt AMPS and thus come to being a novel kind of ionic liquid ZIW/AMPS. As this novel ionic liquid's cations and anions both contain C=C bonds, strong ionic bonds stemming from ionic liquid ZIW/AMPS will exist within or between the poly(ZIW/AMPS)s chains after UV irradiation. Thus, these poly(ZIW/AMPS)s hydrogels combine strong crosslinks and weak crosslinks (ionic bonds). As the special dynamic junctions, the ionic bonds serve as the reversible sacrificial bonds and rupture to dissipate energies under the applied external loading. And the ionic bonds can reform again after removing the external loading. Due to the functional mechanism, these poly(ionic liquid)s hydrogels exhibit high mechanical strength, excellent elongation, and good self-recovery property.

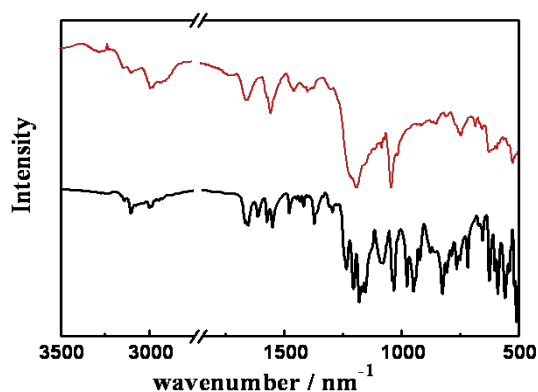


Figure. 2 Comparative FT-IR spectra of ZIW/AMPS (black) and poly(ZIW/AMPS)s (red).

The chemical structures of as-synthesized poly(ZIW/AMPS)s hydrogels were analyzed by the Fourier transform infrared spectra (FT-IR). Fig. 2 shows the FT-IR spectra of ZIW/AMPS and poly(ZIW/AMPS)s. As previously observed, the change in solution consistency to a rubbery solid suggests polymerization of the IL (ZIW+AMPS), to form poly(ZIW+AMPS)s. The disappearance of the vinyl $\nu(-C=C-)$ stretch at 1633 cm⁻¹ is a signature, which is often used to monitor the success of polymerization.⁴⁷ The comparison of the spectrum recorded on the monomer (ZIW+AMPS) to poly(ZIW+AMPS)s shows complete loss of the 1613 cm⁻¹ vibrational mode, confirming that polymerization has been completed. Successful polymerization is further confirmed by the loss of several other bands, including the =CH₂ stretching modes at 3103 cm⁻¹, the =CH₂ deformation mode at 1417 cm⁻¹, =CH₂ rocking modes at 981 cm⁻¹ and =CH bending modes at 949 cm⁻¹. The morphology and microstructure of the hydrogels were investigated by scanning electron microscope (SEM). We can find the porous structure of the hydrogels inside the xerogel (Fig. S1).

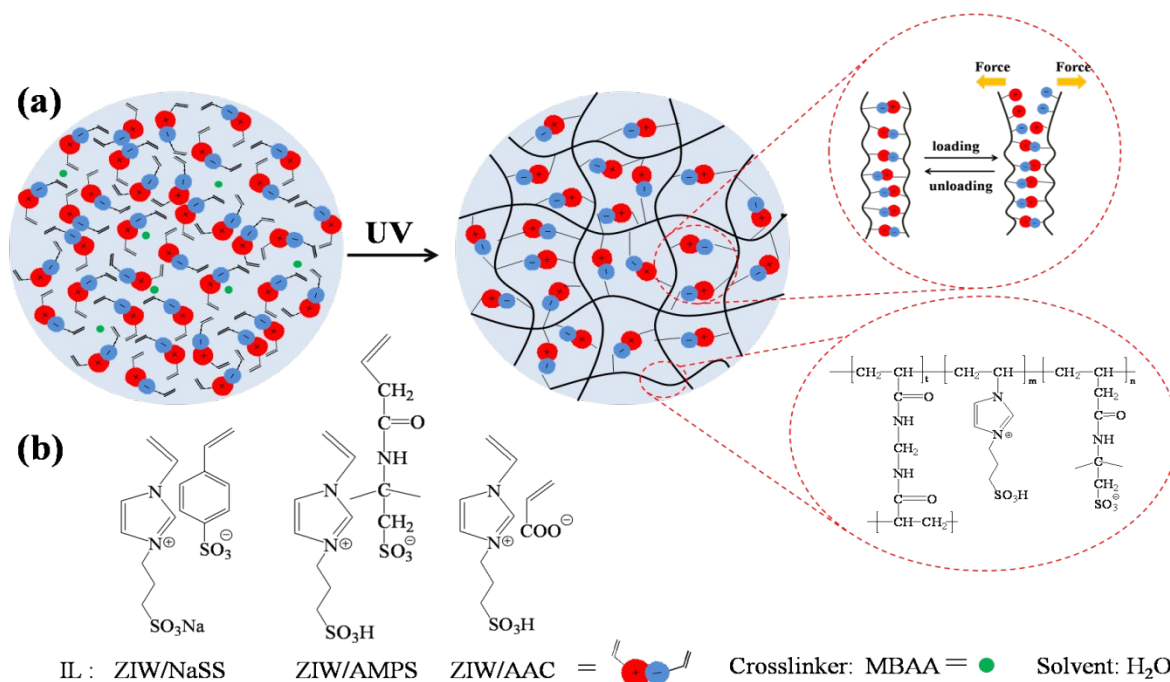


Figure.1 (a) Schematics of poly(ZIW/AMPS) hydrogels: The covalent bonds serve as permanent crosslinking points, and the ionic bonds act as reversible sacrificial bonds that rupture under deformation; (b) The chemical structures of ionic liquids used in this work.

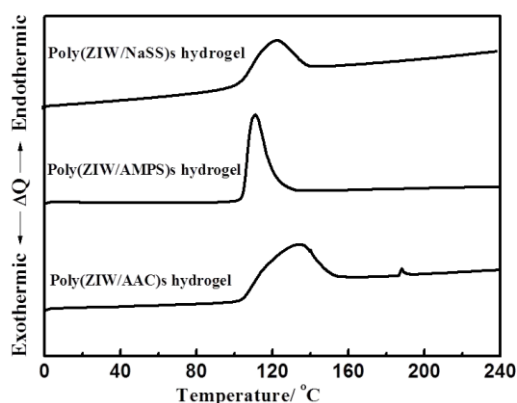


Figure 3 DSC curves of poly(ionic liquid)s hydrogels

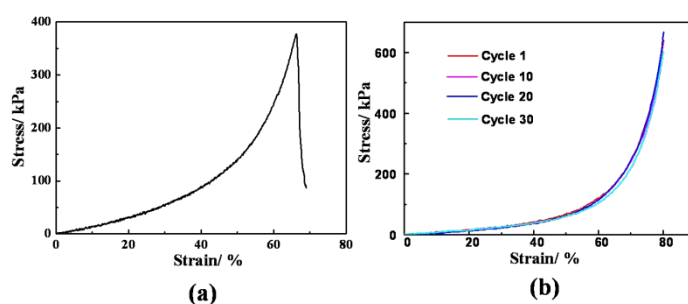
Desirable mechanical and thermal properties are important for flexible electrolytes, especially when they are applied in practical devices. The thermal property of the poly(ZIW/AMPS)s hydrogel electrolyte was characterized by DSC. From the DSC curve (Fig. 3), there is no exothermic peak below 100 °C, indicating the poly(ZIW/AMPS)s hydrogel electrolyte can remain a gel state under 100 °C. The only exothermic peak corresponds to the evaporation of water. As we supposed above, these poly (ZIW/AMPS)s hydrogels, whose cations and anions have been polymerized, indeed exhibit superior mechanical characterization. As shown in Fig. S2, these poly (ZIW/AMPS)s hydrogels can withstand high-level deformations of bending (Fig. S2a), compression (Fig. S2b), and elongation (Fig. S2c) without any visible damage. Particularly, after removing the deformation force, the poly (ZIW/AMPS)s hydrogels can quickly be recovered to their initial shapes, indicating that these hydrogels exhibit excellent self-recovery property.

Table 1 The mechanical properties of hydrogels with various compositions

Amount of components		Mechanical properties (kPa)	
Ionic Liquid	MBAA/mol%	Young's modulus	Compressive strength
ZIW/AMPS	2mol L ⁻¹ 1	15.9	266.0
ZIW/AMPS	3mol L ⁻¹ 0.5	2.6	68.4
ZIW/AMPS	3mol L ⁻¹ 1	42.5	557.0
ZIW/AMPS	3mol L ⁻¹ 1.5	70.5	443.9
ZIW/AMPS	3mol L ⁻¹ 2	134.1	--
ZIW/AMPS	4mol L ⁻¹ 1	75.8	639.9
ZIW/AMPS	5mol L ⁻¹ 1	173.0	1733.0
ZIW/AAC	4mol L ⁻¹ 1	37.5	604.4
ZIW/NaSS	4mol L ⁻¹ 1	224.6	2190.0

To quantitatively examine the mechanical properties of these poly (ZIW/AMPS)s hydrogels, we performed a series of compressive

tests in response to the changes in amounts of components. The effects of different polymerization conditions on the mechanical properties are summarized in Table 1. Taking hydrogels with 3 mol L⁻¹ ZIW/AMPS as an example, as the amount of MBAA increases from 0.5 mol% to 1.5 mol%, the value of compressive strength at 80% strain quickly increases from 68.4 kPa to 557.0 kPa and then decreases to 443.9 kPa. While the amount of MBAA increases to 2 mol%, these hydrogels are destroyed at about 65% strain (Fig.4a), suggesting the hydrogels' flexibilities decrease. These results indicate the optimum content of the crosslinker MBAA is 1 mol%. The mechanical strength of these hydrogels is enhanced with the increase of ZIW/AMPS, the reason of which is that the increase in ZIW/AMPS promotes the density of polymer chains and thus enhances the mechanical strength of the hydrogels. The Young's modulus and compressive strength of the hydrogels with 5 mol L⁻¹ ZIW/AMPS could reach at 173.0 kPa and 1733.0 kPa, respectively. It should not be forgettable that designability is an important feature of ionic liquids.^{22,24,48} Thus we design different kinds of ionic liquids and test their mechanical properties. As shown in Table 1, all these hydrogels show superior mechanical properties and the poly(ZIW/NaSS)s hydrogels rank first among these hydrogels.

Figure 4 (a) Compressive test of hydrogels with 3mol L⁻¹ ZIW/AMPS and 2 mol% MBAA; (b) Compress-recovering nature of poly(ZIW/AMPS)s hydrogels through 40 cycles at a strain of 80%.

That is to say, we could prepare different functional poly(ionic liquid)s hydrogels easily *via* simply changing cations or anions. Fig. 4b shows compress-recovery curves for the poly(ZIW/AMPS)s hydrogels through 30 cycles at a strain of 80%. These hydrogels are self-recoverable after successive and large compressive strain.

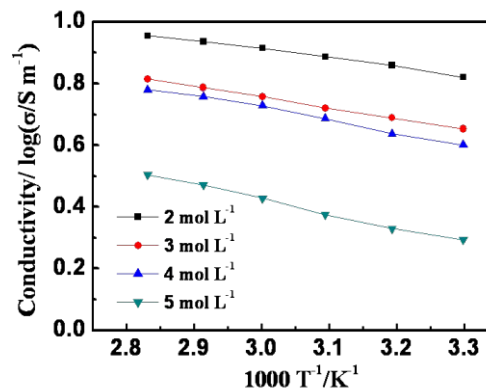


Figure 5 The ionic conductivities of poly(ZIW/AMPS)s hydrogels with various ZIW/AMPS contents and 1 mol% MBAA.

Table 2 electrochemical properties of poly(ZIW/AMPS)s hydrogels with various ZIW/AMPS contents and 1 mol% MBAA

$C_{(\text{ZIW/AMPS})}$, mol L ⁻¹	σ_{30} , S m ⁻¹	Activation Energy/kJ mol ⁻¹
2	6.61	2.36
3	4.45	2.89
4	3.99	3.31
5	1.96	3.90

σ_{30} : ionic conductivity of poly(ZIW/AMPS)s hydrogels in 30°C

Apart from the superior mechanical property, the hydrogels based on poly(ZIW/AMPS)s exhibit excellent electrical properties. By using the alternating current impedance method, we measured the ionic conductivities of poly(ZIW/AMPS)s hydrogels with various contents of poly(ZIW/AMPS)s, and their ionic conductivities are higher than 1 S m⁻¹ at room temperature, which exceed the conductivities of most conducting electrolytes.⁴⁹⁻⁵¹ Along with the increase of ZIW/AMPS content, the ionic conductivity decreases slightly to 1.96 S m⁻¹, which results from the decline of water content. The decrease of water content results in the decrease of mobility of ionic and thus ionic conductivity. It is certified by the activation energy calculated by Arrhenius plots of the conductivity (Fig. 5). In general, the activation energy is regarded as the energy obstacle that the migration of ions must overcome. The smaller the activation energy is, the easier the movement of ion is.^{52,53} As shown in Table 2, the activation energies increase from 2.36 kJ mol⁻¹ to 3.90 kJ mol⁻¹ as the ZIW/AMPS contents increase from 2 mol L⁻¹ to 5 mol L⁻¹, suggesting the decrease of ionic mobility.

In order to look more accurately at the conductivity, Wagner polarization test was performed (Fig. S3). When a fixed small potential (300 mV) was added between the two metallic electrodes, the initial current stemmed from the ion displacement and to the electronic flow simultaneously. However, due to the blocking electrodes effect, the ion displacement decreased with time dramatically, whereas the electronic flow maintained constant during the whole test.⁵⁴ So initial total current (I_T) is the sum of ionic (I_i) and electronic (I_e) currents ($I_T = I_i + I_e$), and the final current is only the electronic current (I_e). The ionic transference number (t_i) was calculated using the relation:

$$t_i = I_i / I_T = (I_T - I_e) / I_T$$

In this test, the ionic transference number is calculated as 96%, suggesting that the charge transport in the poly(ionic liquid)s electrolyte is predominantly accompanied by the ion displacement, and electronic conductivity is negligible.⁵⁵

The stability of electrical properties of the poly(ZIW/AMPS)s hydrogels under mechanical strain were demonstrated by bending tests. Fig. 6 shows the result of bending test of poly(ZIW/AMPS)s hydrogel electrolytes with 4 mol L⁻¹ ZIW/AMPS and 1 mol% MBAA. The poly(ZIW/AMPS)s hydrogel electrolyte shows good mechanical stability during the bending tests in which the conductivities of poly(ZIW/AMPS)s hydrogel electrolytes remain almost constant under different bending angle, that is, 45°, 90°, 135°

and 180° (Fig. 6a). The conductivities of poly(ZIW/AMPS)s hydrogel electrolytes can also maintain about 4 S m⁻¹ up to 1000 bending cycles as shown in Fig. 5b. The electrical stability of poly(ZIW/AMPS)s hydrogel electrolytes was supported by their superior mechanical strength and flexibility.⁵⁶

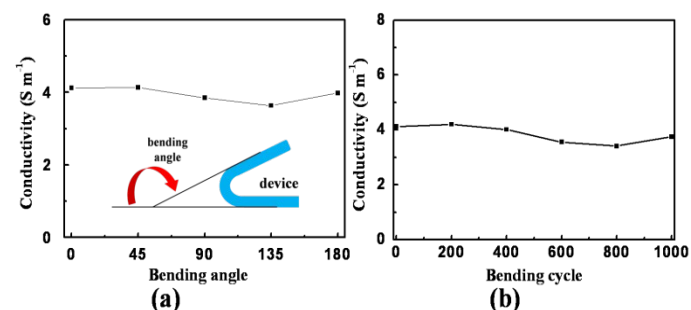


Figure 6 (a) Conductivities of poly(ZIW/AMPS)s hydrogels under different bending states. (b) Conductivities of poly(ZIW/AMPS)s hydrogels after different bending cycles.

To further demonstrate the mechanical stability of poly(ZIW/AMPS)s hydrogel electrolytes, we designed a complete circuit composed of a LED bulb with a electrochemical station as the electrical load, poly(ZIW/AMPS)s hydrogels as the conductor. As shown in Fig. S4, the poly(ZIW/AMPS)s hydrogel electrolyte was sandwiched by two stainless plants, then the LED bulb and the power source were linked into the circuit by copper wires. The bulb was successfully lighted when the circuit was switched to close status. Notably, Fig. S5 shows that this circuit could work well under compressed, bended, folded and twisted states, indicating the outstanding stability of electrical properties of the poly(ZIW/AMPS)s hydrogel electrolytes under mechanical strain.

Conclusion

In summary, one-step synthesis of poly(ionic liquid)s hydrogel electrolytes is reported. Both cations and anions of these ionic liquids contain carbon-carbon double bonds and can be polymerized. To the best of our knowledge, this is the first work of preparing hydrogels based on poly(ionic liquid)s with polymerized cations and anions. The presence of strong and weak crosslinks makes these hydrogels tough, stretchable, flexible and self-recovery. Notably, these poly(ZIW/AMPS)s hydrogels exhibit superior electrochemical properties, which can stay stable under different bending angles and successive bending, folding, compressing and twisting. We believe that these poly(ionic liquid)s hydrogel electrolytes will facilitate the development of high-performance flexible energy storage and conversion devices and thus boost the advent of next-generation flexible electronic devices.

Acknowledgments

The authors are grateful to the National Basic Research Program (2013CB834505), the Specialized Research Fund for Doctoral Program of Higher Education of China (No.20120131130003), the Shandong Provincial Natural Science Foundation, China (ZR2012BZ001).

Reference

- B. D. Gates, *Science*, 2009, **323**, 1566-1567.
- S. Bauer, *Nat. Mater.*, 2013, **12**, 871-872.
- X. F. Wang, X. H. Lu, B. Liu, D. Chen, Y. X. Tong and G. Z. Shen, *Adv. Mater.*, 2014, **26**, 4763-4782.
- D. H. Kim, Y. S. Kim, J. Wu, Z. Liu, J. Song, H. S. Kim, Y. Y. Huang, K. C. Hwang and J. A. Rogers, *Adv. Mater.* 2009, **21**, 3703-3707.
- C. Y. Wang and G. G. Wallace, *Electrochimica Acta*, 2015, **175**, 87-95.
- X. H. Lu, M. H. Yu, G. M. Wang, Y. X. Tong and Y. Li, *Energy Environ. Sci.*, 2014, **7**, 2160-2181.
- P. H. Yang and W. J. Mai, *Nano Energy*, 2014, **8**, 274-290.
- Y. H. Hu and X. L. Sun, *J. Mater. Chem. A*, 2014, **2**, 10712-10738.
- G. M. Zhou, F. Li and H. M. Cheng, *Energy Environ. Sci.*, 2014, **7**, 1307-1338.
- H. Gwon, J. Hong, H. Kim, D. H. Seo, S. Jeon and K. Kang, *Energy Environ. Sci.*, 2014, **7**, 538-551.
- Q. H. Lia, J. H. Wu, Z. Y. Tang, Y. M. Xiao, M. L. Huang and J. M. Lin, *Electrochimica Acta*, 2010, **55**, 2777-2781.
- K. S. Lee, H. K. Lee, D. H. Wang, N. G. Park, J. Y. Lee, O. O. Park and J. H. Park, *Chem. Commun.*, 2010, **46**, 4505-4507.
- K. Rana, J. Singh and J. H. Ahn, *J. Mater. Chem. C*, 2014, **2**, 2646-2656.
- S. Tominaka, H. Nishizeko, J. Mizuno and T. Osaka, *Energy Environ. Sci.*, 2009, **2**, 1074-1077.
- W. Cai, T. Lai, W. Dai and J. Ye, *J. Power Sources*, 2014, **255**, 170-178.
- J. Liu, Z. He, J. W. Xue and T. T. Tan, *J. Mater. Chem. B*, 2014, **2**, 2478-2482.
- B. Lin, L. Qiu, J. Lu and F. Yan, *Chem. Mater.*, 2010, **22**, 6718-6725.
- X. L. Wang and G. Q. Shi, *Energy Environ. Sci.*, 2015, **8**, 790-823.
- H. Wang, G. Wang, Y. Ling, F. Qian, Y. Song, X. Lu, S. Chen, Y. Tong and Y. Li, *Nanoscale*, 2013, **5**, 10283-10290.
- W. Cai, T. Lai, W. Dai and J. Ye, *J. Power Sources*, 2014, **255**, 170-178.
- L. Li, Z. Wu, S. Yuan and X. B. Zhang, *Energy Environ. Sci.*, 2014, **7**, 2101-2122.
- L. A. Blanchard, D. Hancu, E. J. Beckman and J. F. Brennecke, *Nature*, 1999, **399**, 28-29.
- D. R. MacFarlane, M. Forsyth, P. C. Howlett, J. M. Pringle, J. Z. Sun, G. Annat, W. Neil and E. I. Izgorodina, *Acc. Chem. Res.*, 2007, **40**, 1165-1173.
- J. Dupont, R. F. D. Souza, and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667-3692.
- M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nature Materials*, 2009, **8**, 621-629.
- D. Wei and T. W. Ng, *Electrochemistry Communications*, 2009, **11**, 1996-1999.
- P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Grätzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166-1167.
- W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun.*, 2002, 374-375.
- J. Y. Yuan and M. Antonietti, *Polymer*, 2011, **52**, 1469-1482.
- J. Y. Yuan, D. Mecerreyes and M. Antonietti, *Progress in Polymer Science*, 2013, **38**, 1009-1036.
- J. N. Guo, C. Yuan, M. Y. Guo, L. Wang and F. Yan, *Chem. Sci.*, 2014, **5**, 3261-3266.
- C. Yuan, J. N. Guo, Z. H. Si and F. Yan, *Polym. Chem.*, 2015, **6**, 4059-4066.
- X. J. Chen, Q. Li, J. Zhao, L. H. Qiu, Y. G. Zhang, B. Q. Sun and F. Yan, *Journal of Power Sources*, 2012, **207**, 216-221.
- H. Srour, O. Ratel, M. Leocmach, E. A. Adams, S. Denis-Quanquin, V. Appukkuttan, N. Taberlet, S. Manneville, J.-C. Majesté C. Carrot, C. Andraud and C. Monnereau, *Macromol. Rapid Commun.*, 2015, **36**, 55-59.
- Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang and X. Duan, *ACS Nano*, 2013, **7**, 4042-4049.
- N. A. Choudhury, S. K. Prashant, S. Pitchumani, P. Sridhar and A. K. Shukla, *J. Chem. Sci.*, 2009, **121**, 647-654.
- J. P. Gong, *Soft Matter*, 2010, **6**, 2583-2590.
- C. W. Peak, J. J. Wilker and G. Schmidt, *Colloid Polym Sci*, 2013, **291**, 2031-2047.
- J. Y. Sun, X. H. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. G. Suo, *Nature*, 2012, **489**, 133-136.
- K. J. Henderson, T. C. Zhou, K. J. Otim and K. R. Shull, *Macromolecules*, 2010, **43**, 6193-6201.
- P. Lin, S. H. Ma, X. L. Wang, and F. Zhou, *Adv. Mater.*, 2015, **27**, 2054-2059.
- T. L. Sun, T. Kurokawa, S. Kuroda, A. B. Ihsan, T. Akasaki, K. Sato, Md. A. Haque, T. Nakajima and J. P. Gong, *Nature Materials*, 2013, **12**, 932-937.
- A. B. Ihsan, T. L. Sun, S. Kuroda, Md. A. Haque, T. Kurokawa, T. Nakajima and J. P. Gong, *J. Mater. Chem. B*, 2013, **1**, 4555-4562.
- X. H. Liu, Z. B. Wen, D. B. Wu, H. L. Wang, J. H. Yang and Q. G. Wang, *J. Mater. Chem. A*, 2014, **2**, 11569-11573.
- H. Park, H. S. Kim and Y. M. Jung, *J. Phys. Chem. B*, 2011, **115**, 1743-1750.
- X. P. Gao, F. Lu, B. Dong, T. Zhou, Y. Z. Liu and L. Q. Zheng, *RSC Adv.*, 2015, **5**, 63732-63737.
- B. G. Wall and J. L. Koenig, *Appl. Spectrosc.*, 1997, **51**, 1453-1459.
- H. Xua, Z. Han, D. J. Zhang and C. B. Liu, *Journal of Molecular Catalysis A: Chemical*, 2015, **398**, 297-303.
- C. Laberty-Robert, K. Vallé F. Pereira and C. Sanchez, *Chem. Soc. Rev.*, 2011, **40**, 961-1005.
- T. Ichikawa, T. Kato and H. Ohno, *J. Am. Chem. Soc.*, 2012, **134**, 11354-11357.
- Shalu, V. K. Singh and R. K. Sing, *J. Mater. Chem. C*, 2015, **3**, 7305-7318.
- A. Garc ía, L. C. Torres-González, K. P. Padmasree, M. G. Benavides-Garcia and E. M. Sánchez, *J. Mol. Liq.*, 2013, **178**, 57-62.
- T. P. Huang, N. Q. Tian, Q. Y. Wu and W. F. Yan, *Soft Matter*, 2015, **11**, 4481-4486.
- J.-B. Ducros, N. Buchtova, A. Magrez, O. Chauvet and J. Le Bideau, *J. Mater. Chem.*, 2011, **21**, 2508-.
- D. Saikia and A. Kumar, *Electrochimica Acta*, 2004, **49**, 2581-2589.
- Y. Shi, M. Wang, C. B. Ma, Y. Q. Wang, X. P. Li and G. H. Yu, *Nano Lett.*, 2015, **15**, 6276-6281.