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Stretchable alkaline *quasi*-solid-state electrolytes created by super-tough, fatigue-resistant and alkali-resistant multi-bond network hydrogels

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ABSTRACT

Hydrogel-based *quasi*-solid-state electrolytes (Q-SSEs) swollen with electrolyte solutions are important components in stretchable supercapacitors and other wearable devices. This work fabricates a super-tough, fatigue-resistant, and alkali-resistant multi-bond network (MBN) hydrogel aiming to be an alkaline Q-SSE. To synthesize the hydrogel, a 2-ureido-4[1*H*]-pyrimidone (UPy) motif is introduced into a poly(acrylic acid) polymer chain. The obtained MBN hydrogels with 75 wt% water content exhibit tensile strength as high as 2.47 MPa, which is enabled by the large energy dissipation ability originated from the dissociation of UPy dimers due to their high bond association energy. Owing to the high dimerization constant of UPy motifs, the dissociated UPy motifs are able to partially re-associate soon after being released from external forces, resulting in excellent fatigue-resistance. More importantly, the MBN hydrogels exhibit excellent alkali-resistance ability. The UPyGel-10 swollen with 1 mol/L KOH display a tensile strength as high as ~1.0 MPa with elongation at break of ~550%. At the same time, they show ionic conductivity of ~17 mS/cm, which do not decline even when the hydrogels are stretched to 500% strain. The excellent mechanical property and ionic conductivity of the present hydrogels demonstrate potential application as a stretchable alkaline Q-SSE.

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In modern society, flexible electronic devices such as wearable devices and electronic skins have been attracting wide researching interest because of their convenience and real-time monitoring of human health [1–5]. Many efforts have been done to develop high-strength flexible polymer materials with attractive properties, satisfying the demand of self-healing, adhesiveness, and recyclability [6–10]. Besides the matrix materials, stretchable supercapacitors (SSCs) are the very basic structure units inside the flexible electronic devices, which are composed of a layer of electrolyte sandwiched by two electrodes [11,12]. To achieve high stretchability of the conventional supercapacitors, except of the stretchable electrodes, the electrolyte must have the following properties: high tensile strength, large elongation at break and high electronic or ionic conductivity.

Hydrogels are soft materials swollen with a large amount of water or aqueous solution. It has been well acknowledged that inhomogeneous networks and lack of energy dissipation mechanism are the two intrinsic obstacles that usually make hydrogels weak in mechanical properties [13]. To overcome these shortcomings, researchers have developed two kinds of methodologies to make tough hydrogels. One is the double network (DN) strategy [14,15], and the other is multi-bond network (MBN) strategy [16–28], which involves a single network crosslinked by hierarchical interactions (chemical bonds and dynamic bonds such as hydrogen bonds, hydrophobic interactions and ionic bonds) with different bond association energy, and fabricated a series of super-tough hydrogels. These hydrogels exhibited very balanced mechanical properties: excellent tensile strength (up to 6.95 MPa) and large elongation at break (up to 3000%). By swelling the hydrogels with acidic, saline or alkaline aqueous solution to enhance the ionic conductivity, one can obtain hydrogel-based quasi-solid-state electrolytes (Q-SSEs), which are good electrolyte candidates for the fabrication of SSCs. Based on the MBN strategy, we have successfully fabricated poly(acrylic acid) (PAA)/H_3PO_4 and polyacrylamide (PAM)/H_3PO_4 MBN hydrogel-based Q-SSEs to assemble self-healable SSCs, which exhibited both excellent mechanical and electrical properties [29,30]. Among the Q-SSEs, alkali-resistant hydrogel electrolytes are vital for the advancement of SSCs because a series of high-capacitive electrode materials, such as NiO [31,32], $NiCo_2O_4$ [33–35], and Fe_2O_3 [36–38], can only work under alka-

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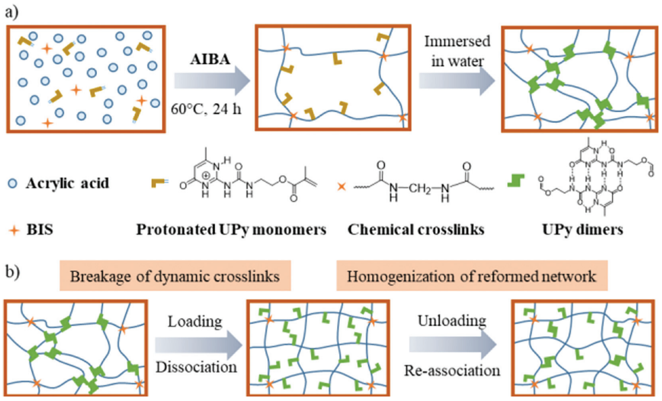

Fig. 1. (a) Synthetic schemes of the MBN hydrogels. (b) An illustration of network homogenization after loading-unloading cycle: UPy dimers are dissociated when hydrogels are exerted to external forces. Once released from external forces, UPy dimers are able to partially re-associate in a more homogeneous manner.

line conditions [39]. Therefore, it is of great importance to fabricate alkali-resistant, super-tough hydrogels aiming to be used as alkaline Q-SSEs.

The 2-ureido-4[1*H*]-pyrimidone (UPy) unit shows a well-defined self-complementary dimerization through quadruple hydrogen bonding, which displays a high dimerization constant ($>10^5$ L/mol in chloroform) [40], and has been intensively investigated to fabricate tough hydrogels [41]. The UPy dimers are relatively stable under alkaline condition and have a high bond association energy ($\Delta G \approx 70$ kJ/mol) [42]. Recently, we incorporated UPy motifs to fabricate MBN hydrogels [27], which showed excellent energy dissipation ability and rapid self-recovery ability due to the high dimerization constant and high bond association energy.

In this work, to investigate the feasibility of the UPy-contained MBN hydrogels fabricated by the acid-aided method being applied as a stretchable alkaline Q-SSE, the fatigue-resistance and the alkaline-resistance are investigated. Moreover, the ionic conductivity of the hydrogels swollen with KOH solution (75 wt% water content) are evaluated.

The hydrogels are fabricated in a process as shown in Fig. 1a. The aromatic ring of the UPy monomers is protonated under acidic condition to restrain the dimerization, resulting in highly water-soluble protonated UPy monomers [27]. Successively, the copolymerization between AA and the protonated vinyl-hybrid UPy monomer is initiated by 2,2′-azobis[2-methylpropionamidine] dihydrochloride (AIBA) at 60 °C, using a slight amount of BIS (0.1 mol% with respect to AA) as the crosslinker. The obtained sparsely crosslinked hydrogels are then immersed in a large amount of water, which is refreshed every 4 h (total 3 times) for the complete removal of excess HCl. With the increase of pH values, UPy dimers are formed due to deprotonation of UPy motifs, resulting in dense dynamic crosslinks as shown in Fig. 1a. The obtained MBN hydrogels have one single network (PAA network) with two categories of interactions: sparse covalent crosslinks (*i.e.*, BIS) and two types of dynamic crosslinks (regular hydrogen bonds among PAA chains and quadruple hydrogen bonds within UPy dimers). When exerted to external forces, dynamic crosslinks will break to dissipate energy, while the sparse covalent crosslink helps maintain the integrity of the network, thus the UPy-based MBN hydrogels are expected to exhibit excellent mechanical properties. These hydrogels are denoted as UPyGel-*x*, where *x* stands for the molar ratios of UPy monomer with respect to AA.

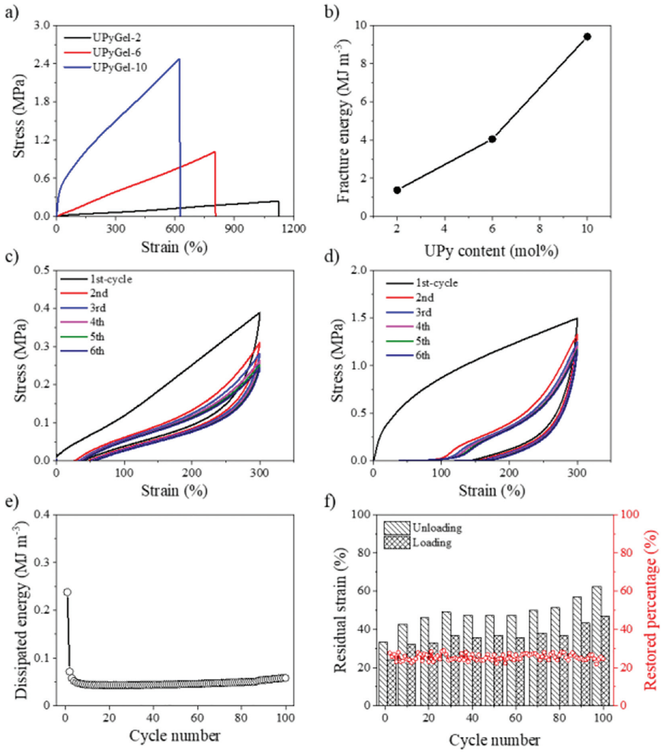

Fig. 2. (a) Stress-strain curves of the UPyGels with different amount of UPy motifs, and (b) fracture energy of the UPyGels as a function of UPy content. Fatigue resistance: 6 cycles of loading-unloading tensile tests of (c) UPyGel-6 and (d) UPyGel-10. 100 cycles of loading-unloading tensile tests of UPyGel-6: (e) dissipated energy and (f) residual strain of every ten cycles and its restoring, as functions of cycle number.

Mechanical property is the most vital criterion to judge the practicability of a Q-SSE material to be used in flexible electronic devices. Therefore, first of all, the effect of UPy content on the mechanical properties of the UPyGels (water content is fixed at 75 wt%) is investigated by varying the feed molar ratio of UPy monomers. Similar to our previous work [27], the tensile strength increases as the increase of UPy content (Fig. 2a). An extremely high tensile strength of ~2.3 MPa is achieved when the UPy content is 10 mol%, which is 10 times as that of UPyGel-2 (0.24 MPa). This great enhancement in mechanical strength is mainly due to the effective energy dissipation enabled by the dissociation of UPy dimers when the hydrogels are stretched [27]. The total energy dissipated during the whole stretching process is calculated from the integral area under each stress-strain curve. This energy is called fracture energy, which evaluates the toughness of materials. The fracture energy of the hydrogels drastically increases as the increase of UPy content and reaches nearly 10 MJ/m^3 for UPyGel-10 (Fig. 2b), which is comparable to common ionic hydrogels [18,22]. The elongation at break decreases from 1122% to 623% as the increasing of UPy content from 2 mol% to 10 mol%, which is ascribed to the increasing crosslinking density of the UPy dimers. However, even at a UPy content as high as 10 mol%, the UPyGel-10 sample still exhibits a high stretchability.

Besides the mechanical properties, fatigue resistance is also an important criterion for the practicability of a Q-SSE, because this material is usually applied under frequent stretching and releasing cycles. This application situation is simulated by 6 cycles of loading-unloading tensile tests to show the fatigue resistance (Figs. 2c and d). It clearly shows a large hysteresis loop in the first cycle, which indicates that a massive amount of energy is dissipated from the dissociation of UPy dimers. It is known that if the dissociated interaction cannot re-associate (*e.g.*, covalent bonds), no hysteresis loop will appear in the second cycling test [43–45]. However, similar to other ionic MBN hydrogels [18,22,25], the immediate second cycling tensile test of the UPyGels still shows a pronounced hysteresis loop, which is ascribed to the partial re-association of the dissociated UPy dimers. This quick re-association rate is ascribed to the high dimerization constant of UPy motifs. Moreover, when extra cycling tensile tests are conducted, the hysteresis loops nearly overlap with each other, indicating that the hydrogels exhibit excellent fatigue resistance ability. The partially re-associated UPy dimers continuously break and re-associate during the loading-unloading cycles, resulting in a dynamic equilibrium network, without any collapse of the network structure. Next, 100 cycles are conducted on UPyGel-6 to further demonstrate the fatigue resistance ability. The integral area of the hysteresis loop is calculated and plotted in Fig. 2e, which reflects the dissipated energy. It clearly shows that except the first cycle, the dissipated energy almost does not decline and even slightly increases. The slight increase in dissipated energy indicates that the network becomes more homogeneous after the repeating dissociation and re-association of UPy dimers, which will be discussed in more detail later. Moreover, the dissociation of UPy dimers also leads to obvious residual strains in every unloading step due to the deformed network. After the UPy dimers partially re-associate, the residual strain partially restores at the next loading step (Fig. 2f). The restored percentage of residual strain is calculated according to Eq. S2 (Supporting information), and it is found that the residual strain remains in the range of 20%–30%, which also indicates a dynamic equilibrium network and an excellent fatigue resistance ability endowed by the effective dissociation-re-association of UPy dimers.

The network homogenization can be further demonstrated by a gradient loading-unloading tensile test with gradually increasing maximum strain until the hydrogels are broken (Fig. S2 in Supporting information). It can be seen that for both UPyGel-6 and UPyGel-10, the maximum stress of each loading-unloading cycle locates on the stress-strain curves of the uniaxial tensile test, which again demonstrates that the dynamic network does not collapse during the loading-unloading process because of the quick re-association rate of UPy dimers. Moreover, due to the repeated dissociation and re-association of UPy dimers, a more homogeneous network is generated, resulting in both a higher tensile strength and a larger elongation at break in the gradient tensile test than those in the uniaxial tensile test. A possible mechanism for the network homogenization is illustrated in Fig. 1b. In fact, during the deprotonation step when fabricating UPyGels, UPy dimers formed randomly in the hydrogel network in the beginning, resulting in an inhomogeneously crosslinked network. When the hydrogels are exerted to external forces, the UPy dimers are dissociated to dissipate energy. During the unloading process, part of the dissociated UPy motifs can immediately re-dimerize with the adjacent dissociated ones due to the high dimerization constant, facilitating a more homogeneous network.

To fabricate an alkaline Q-SSE, the hydrogels must have adequate mechanical strength under alkaline conditions. The alkali-resistance of UPyGels can be demonstrated by a swelling experiment in KOH aqueous solutions with different concentrations (10^{-4}–1 mol/L). If the crosslinking points are sensitive to alkali, the network will collapse after swelling with KOH solutions. The time-dependent swelling ratio of UPyGel-10 (calculated from Eq. S1 in Supporting information) is shown in Fig. 3. It can be clearly seen that all samples reach swelling equilibrium within 72 h. Due to the stability of UPy dimers under alkaline conditions, the swelling behavior of UPyGel-10 in 10^{-4} mol/L KOH (pH 10) is almost the same as that in pure water. With increasing KOH concentration from 10^{-4} mol/L to 0.01 mol/L (pH from 10 to 12), the equilibrium swelling ratio gradually increases to around 367 g/g. This is because that under alkaline condition, a small part of UPy motifs will be transformed to enolate anions by reaction with KOH [46], so that the amount of UPy dimers decreases, leading to a decline in the crosslinking density. However, the remaining UPy dimers can still provide the MBN hydrogels with an adequate mechanical strength, and the hydrogel (only 0.27 wt% polymer content) can still retain an intact shape (Fig. 3d), demonstrating excellent alkali resistance of the UPy-based MBN hydrogels. With further increase in KOH concentration from 0.01 mol/L to 1 mol/L (pH from 12 to 14), the equilibrium swelling ratio is dominantly affected by the increasing osmotic pressure of the solution, and decreases to 36.3 g/g for 1 mol/L KOH solution. Due to the alkali resistance ability, the sample (only 2.68 wt% polymer content) can still tolerate the compressive force by a microslide (Fig. S3 in Supporting information).

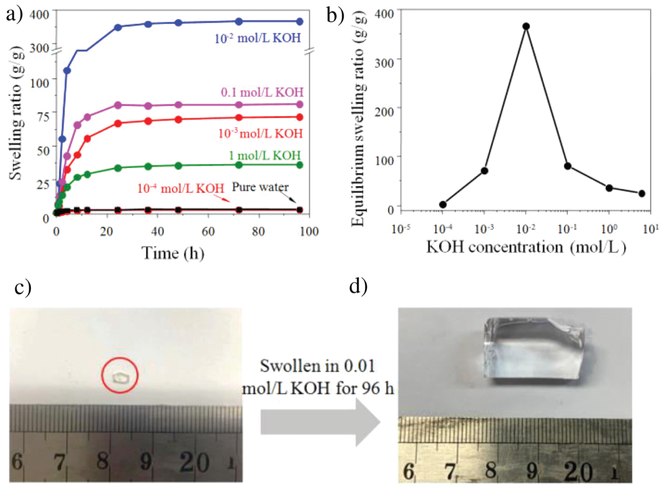

Fig. 3. (a) The swelling behavior of UPyGel-10 in KOH aqueous solutions with different concentrations (10^{-4}–1 mol/L), and (b) equilibrium swelling degree of UPyGel-10 as a function of KOH concentration. (c, d) The UPyGel-10 can swell 367 g/g of 0.01 mol/L KOH aqueous solution and still retain an intact shape.

Ionic conductivity can be endowed to the UPyGels by swelling KOH aqueous solutions. To demonstrate the feasibility of the UPyGels for application as Q-SSEs, the UPyGel-6 and UPyGel-10 dry gels are allowed to absorb given amounts of KOH aqueous solutions with different concentrations (mass ratio of KOH solution to dry gel is 3.0 g/g, ensuring polymer content being 25 wt%) and the mechanical properties are evaluated. As shown in Figs. 4a and b, although both the tensile strength and elongation at break slightly decrease with the increase of KOH concentration, UPyGel-6 swollen with 1 mol/L KOH aqueous solution still exhibit tensile strength of ~0.24 MPa with elongation at break of ~450%, while UPyGel-10 exhibit a higher tensile strength of ~1.0 MPa with a larger elongation at break of ~550%, which can adequately satisfy the application as a Q-SSE in flexible electronic devices [29–30]. The fracture energy of UPyGel-10 in 1 mol/L KOH is still as high as 2.79 MJ/m^3 (black line in Fig. 4e). Besides, The UPyGel-10 in 1 mol/L KOH also exhibit excellent fatigue resistance property. (Figs. 4c and d) The electric resistance of UPyGel-10 in different KOH solutions is measured, from which the ionic conductivity is calculated according to Eq. S3 (Supporting information), which remains around 0.2 mS/cm when KOH concentration is lower than 0.01 mol/L. The conductivity drastically increases when KOH concentration is higher than 0.1 mol/L and reaches ~17 mS/cm at 1 mol/L KOH (red line in Fig. 4e), which is comparable to the most frequently utilized electrolyte systems such as PVA/H_3PO_4 [12,29]. Moreover, because the ionic conductivity mainly originates from the KOH solution, it does not change even when the hydrogels are stretched to 500% strain (Fig. 4f), demonstrating excellent stretchability of the UPyGels. In summary, UPyGel-10 with 1 mol/L KOH exhibits both high mechanical toughness and appropriate ionic conductivity at the same time, which is expected to be an excellent candidate as a stretchable Q-SSE.

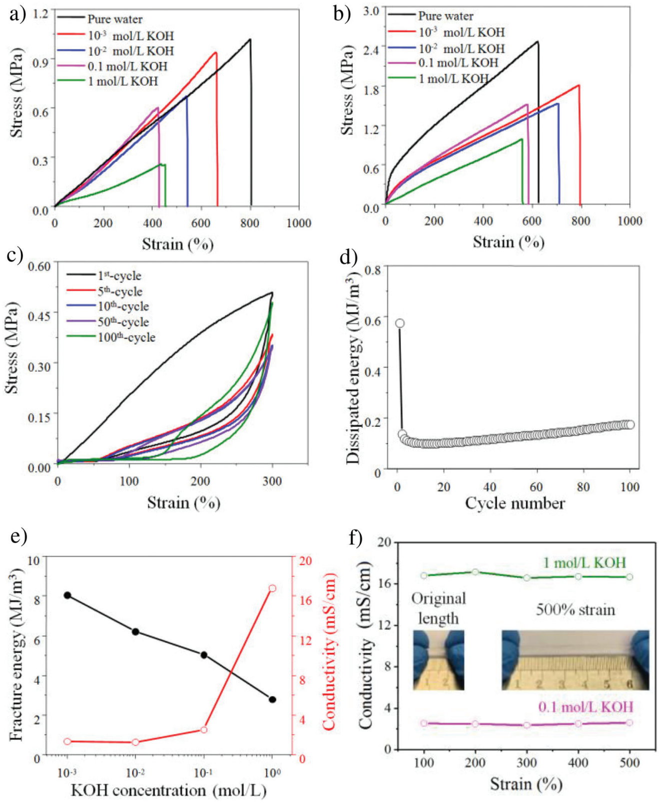

Fig. 4. Stress-strain curves of (a) UPyGel-6 and (b) UPyGel-10 swollen with different KOH solutions (25 wt% polymer content). (c) 100 cycles of loading-unloading tensile tests of UPyGel-10 (swollen with 1 mol/L KOH) and (d) dissipated energy of each cycle. (e) Fracture energy and ionic conductivity of UPyGel-10 as a function of KOH concentration and (f) ionic conductivity change of UPyGel-10 samples (with 1 mol/L and 0.1 mol/L KOH) when they are stretched to 500% strain.

In conclusion, we have fabricated MBN hydrogels with UPy dimers as energy dissipation units in an acidic aqueous solution. The obtained UPyGel-10 (75 wt% water content) exhibits excellent tensile strength as high as 2.47 MPa with an elongation at break of 620% due to the energy dissipation of dissociation of UPy dimers. Owing to the high dimerization constant of UPy motifs, the UPyGels have excellent fatigue resistance and can sustain 100 loading-unloading tensile cycles without decline of the mechanical properties. Moreover, as UPy dimers are relatively stable under alkaline conditions, the UPyGel-10 can swell 367 g/g of 0.01 mol/L KOH without collapsing of the network, indicating excellent alkali resistance of the present MBN hydrogels. When swollen with 3.0 g/g of 1 mol/L KOH, UPyGel-10 (25 wt% polymer content) exhibits both high tensile strength (~1.0 MPa) and high ionic conductivity (~17 mS/cm). The present super-tough, fatigue-resistant, ionic conductive MBN hydrogels demonstrate an excellent potential application as stretchable Q-SSEs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.04.068.

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