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Gangrou Peng

University of Wollongong, gp191@uowmail.edu.au

Yu Ge

University of Wollongong, yg711@uowmail.edu.au

Jie Ding

Land Division, Defence Science And Technology Organisation, jie.ding@dsto.defence.gov.au

Caiyun Wang

University of Wollongong, caiyun@uow.edu.au

Gordon G. Wallace

University of Wollongong, gwallace@uow.edu.au

See next page for additional authors

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Authors

Gangrou Peng, Yu Ge, Jie Ding, Caiyun Wang, Gordon G. Wallace, and Weihua Li

Magnetorheological technology for fabricating tunable solid electrolyte with enhanced conductivity and mechanical property

Gangrou Peng¹, Yu Ge², Jie Ding^{3}, Caiyun Wang², Gordon G. Wallace² and Weihua Li^{1*}*

¹School of Mechanical, Materials, Mechatronics and Biomedical Engineering, University of Wollongong, Northfields Ave, University of Wollongong, NSW 2522, Australia

²ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, University of Wollongong, NSW 2522, Australia

³Land Division, Defence Science and Technology Group, 506 Lorimer Street, Fishermans Bend, VIC 3207, Australia

Abstract

Ionogels are a new class of hybrid materials where ionic liquids are immobilized by macromolecular support. The excessive amount of crosslinking polymer enhances the mechanical strength but compromises the conductivity. Here, we report an elastomeric magnetorheological (MR) ionogel with an enhanced conductivity and mechanical strength as well. Following the application of magnetic nanoparticles into an ionic liquid containing minimum cross-linking agent, **the formation**, thus physical properties, of **MR ionogels are** co-controlled by simultaneously applied UV light and external magnetic field. **The application of MR ionogels as solid electrolytes in supercapacitors is also demonstrated to study electrochemical performance.** This work opens a new avenue to synthesize robust ionogels with the desired conductivity and controllable mechanical properties for soft flexible electronic devices. Besides, as a new class of novel conductive Magneto-rheological elastomers, the proposed MR ionogel also possesses the potential for engineering applications, such as sensors and actuators.

Keywords: magnetorheological technology, ionogels, solid electrolyte, UV

1. Introduction

The use of ionogels as solid electrolytes eliminates the concerns associated with liquid electrolytes while maintaining the physiochemical properties of ionic liquids: negligible vapor pressure, non-flammability, chemical and electrochemical stability, and high conductivity [1-5]. Thus, they have generated extensive interest among novel electronic devices. The development of ionogels leads to a new generation of high performance solid state electrolyte [6]. The preparation of ionogels has been extensively investigated [6-9]. They have demonstrated their applications in solar cells [10], fuel cells [11], batteries [12], transistors [13] and electrochemical double layer capacitors [14].

Highly conductive ionogels can be fabricated using different strategies. Ueno *et al.* proposed mixing silica nanoparticles with ionic liquids (ILs) [15, 16], and the increased content of silica led to gelation eliminating the mixture's ability to flow. However, this ionogel only exhibited a solid-like rheological response, **rather than retaining a defined shape**, and turned into flakes at even higher content of silica nanoparticles. The conductivity dramatically decreased at this gelled state **which** limited the application in electrochemical devices [15]. Fukushima *et al.* [17] proposed grinding carbon nanotubes with imidazolium ion-based ILs. Despite being highly conductive, these bulky gels were merely viscous paste. Even using a polymerizable IL, their mechanical properties were still not satisfactory, as evidenced by an obvious decrease in modulus at a small strain deformation amplitude. In order to generate solid free-standing ionogels with acceptable mechanical strength, different fabrication methods have been proposed, including self-assembly of di-block or tri-block copolymers [18-20], UV or thermal-initiated free radical polymerization [21-23], and sol-gel silica formation [24]. The use of excessive amount of solid support enhances the mechanical strength but compromises the conductivity [25].

Balancing the conductivity and mechanical strength is a critical task in designing high-performance ionogels [26, 27].

Here, we report on utilizing magnetorheology (MR) to generate a novel elastomeric magnetorheological (MR) ionogel with enhanced conductivity and mechanical modulus. The MR effect refers to the reversible formation of orderly alignments of magnetic sensitive micro/nanoparticles dispersed in MR fluids upon the application of an external magnetic field, which leads to significant manipulation of mechanical strength [28-30]. In this study, a solid MR ionogel was prepared by applying a magnetic field and a UV light source simultaneously to a fluid containing silica coated magnetic **nanoparticles and an ionic** liquid with photo-initiated polymerizable agent. A controllable alignment of the chain-like structure was formed under the magnetic field, and was stabilized by illumination of UV light in the MR ionogel. The mechanical and conductive properties of the formed MR ionogels can be tuned by the applied magnetic fields. Unlike conventional MR fluids, this solidification process is irreversible. Even after the magnetic field is removed, the MR ionogel cannot return to its original liquid state, as the solid structure has been permanently generated during the UV crosslinking process. **The alignment structure of magnetic nanoparticles exhibiting sound response** to external magnetic field plays the role of solid support without undermining performance of conductive components. The application of this MR ionogel in supercapacitors is also demonstrated. This work opens a new avenue to synthesize robust ionogels with high conductivity and controllable mechanical properties for soft flexible electronic devices. As a new class of novel conductive Magneto-rheological elastomers (MREs), this MR ionogel may also find potential applications in sensors and actuators.

2. Experimental

Fabrication of MR ionogel samples: The chemicals used in the fabrication of MR ionogel include silica coated iron oxide nanoparticles together with PEGDA (Polyethylene (glycol) Diacrylate Mn=700 Sigma-Aldrich, US), HOMPP (2-Hydroxy-2-methylpropiophenone $\geq 97\%$ Sigma-Aldrich, US), EMITFSI (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $\geq 98\%$ HPLC Sigma-Aldrich, US) and PEO (Polyethylene Oxide Mv=4,000,000, powder Sigma-Aldrich, US).

Base ionogel/or ionogel A was generated by mixing 8 wt % of PEGDA, 3 wt% of HOMPP with EMITFSI, and Ionogel B and C were fabricated with addition of PEO, 1 wt % and 3 wt%, respectively. The weight ratios were with respect to EMITFSI. The precursors were exposed to a UV light source (6000 mW/cm²) for 10 minutes for the solidification.

The MR ionogels samples were generated by adding 10 wt % of silica coated iron oxide nanoparticles into ionogel A, B and C precursors to obtain MR ionogel A₀, B₀ and C₀. The mixtures were cured under both a UV light source (6000 mW/cm²) and a magnetic field of 60 mT, 120 mT or 240 mT for an hour to obtain the MR ionogels A₆₀, A₁₂₀ and A₂₄₀, MR ionogel B₆₀, B₁₂₀ and B₂₄₀, MR ionogel C₆₀, C₁₂₀ and C₂₄₀. **A table summarizing the composition and preparation condition is included in supporting information (Table S1).**

Optical observation: A Leica M205A optical microscopy was used to observe the microstructure of MR ionogel samples at a magnification rate of 200.

Rheological experiments: Steady shear tests and dynamic oscillatory shear tests were carried out using an Anton Parr MCR 301 rheometer with a parallel plate configuration. An external magnetic field of the desired intensity was applied to the samples for two minutes before the test to ensure that the MR ionogels were fully activated. A strain deformation was then applied to the

samples and increased logarithmically from 0.001% to 1000%; the magnetic field remained active during the shearing process.

Ionic conductivity measurement: The ionic conductivity of ionogel matrix or MR ionogels were determined with AC impedance using a Gamry EIS 3000 system in the frequency range of 0.01 Hz to 10 kHz. These samples (20 mm diameter disc, 1 mm thickness) were sandwiched between two quadrilateral gold mylar electrodes. A field-on conductivity test was also carried out with a pair of permanent magnets placed on both sides of samples providing constant field strength of 100 mT.

Assembly of supercapacitors using MR ionogels: The cells were assembled by sandwiching MR ionogels A₀, A₁₅₀ and A₃₀₀, between two active carbon (AC) electrodes. The AC electrode was composed of commercial active carbon (Cap-xx Ltd, Australia) (80 wt%), carbon black (10 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone. The resultant slurry was coated onto an aluminum foil substrate and dried at 80 °C for 12 h in a vacuum oven. The thickness of the MR ionogel used as solid electrolyte was set at 0.65 mm, and the area of AC electrodes was 1 cm × 1 cm.

Electrochemical characterizations: The CV tests of the supercapacitors were conducted from 0.0–3.0 V using a CHI 604D electrochemical analyzer (CHI Instruments) at a scan rate of 50 mV/s. The galvanostatic charge/discharge tests were performed using a LAND CT2001A battery test system at a potential window of 0.005–3.000 V.

3. Results and Discussion

Magnetic properties and an absence of redox activity are the essential requirements for the nanoparticles used to generate MR based electrolytes. The dispersible magnetic particles, Fe₃O₄

coated with a layer of silica were used in this work (FigureS1 of supporting information). This silica layer improved the dispersion stability of the magnetic nanoparticles in the IL [31]. It also insulated the redox activity of the Fe_3O_4 nanoparticles, as demonstrated in our previous report [32].

To obtain MR ionogel, the silica coated magnetic particles were introduced to a widely-studied base ionogel to form a reinforced structure. The fabrication process of MR ionogel is presented in Figure 1a, where a precursor liquid which contained the matrix of base ionogel and magnetic particles (as described in the experiment part) were placed between a pair of electromagnets and UV light source. The magnetic structure transforms from a random distribution to an orderly alignment upon the application of an external magnetic field and is stabilized by the illumination of UV light, as illustrated in the schematic structure of MR ionogel (Figure 1b). A typical base ionogel without magnetic particles is presented in Figure 1c as a free standing flexible and transparent film. As a comparison, a newly synthesized MR ionogel is shown in Figure 1d. The film was fabricated under the external magnetic field and UV light. It forms a flexible and free-standing film, but is non-transparent due to the addition of magnetic nanoparticles.

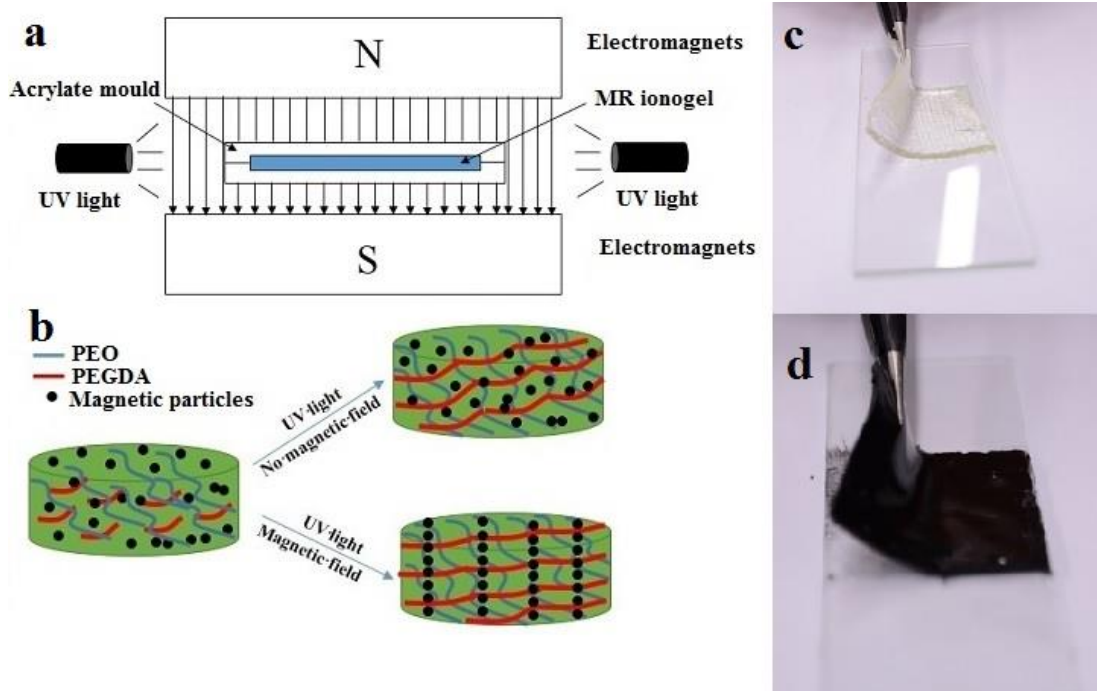


Figure 1. Fabrication of MR ionogel samples (a) Schematic of MR ionogel sample fabrication. (b) Schematic of the formation of MR ionogel sample through photo-initiated method with PEGDA (polyethylene (glycol) Diacrylate) as cross-linking agent and PEO (polyethylene oxide) as added component. (c) Ionogel base matrix sample and (d) MR ionogel sample.

To investigate the effect of polymer addition on the structure of MR ionogel, ionogels A, B and C were prepared from the base matrix of ionogels with 0%, 1% and 3% of PEO addition.

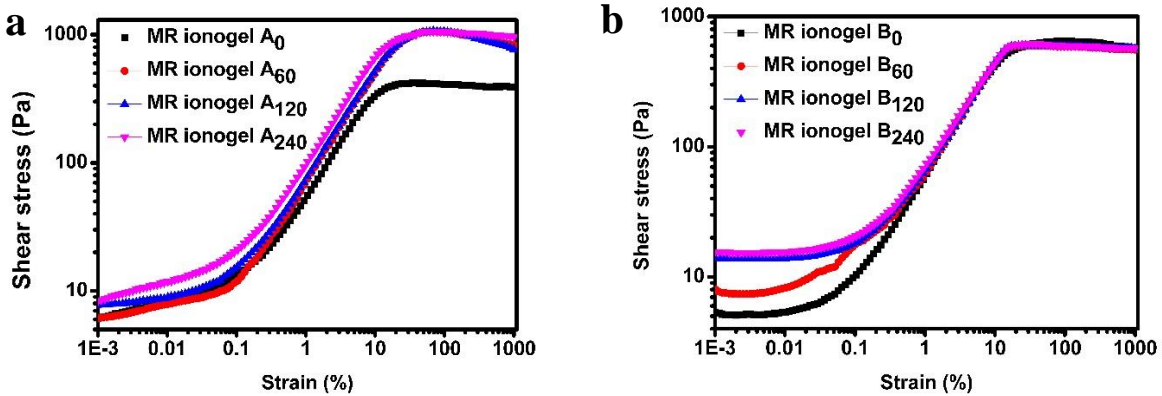
The rheological properties of ionogel matrix samples A, B and C were revealed through steady shear (a), dynamic strain sweep (b), dynamic frequency sweep from 0.01-200 rad/s at constant strain of 1% (c) and 10% (d) are shown in Figure S2 (Supporting Information). Ionogel A and B displayed quite similar rheological properties, until an observable reduction in shear stress and shear modulus was revealed for Ionogel C, indicating a threshold value where PEO addition starts to affect the properties of the samples. As expected [33, 34], the initial shear stress was decreased and the ratio between loss modulus (G'') and storage modulus (G') was increased with

the increased amount of polymer, which demonstrates that high content of polymer leads to a softer and more flexible ionogel due to growing possibility of polymer chain recoil [35].

MR ionogel A₀, B₀ and C₀ were generated by adding 10 wt % of silica coated iron oxide nanoparticles into ionogel A, B and C absence of external magnetic field. More MR ionogel samples were cured under both a UV light source and a magnetic field of 60 mT, 120 mT or 240 mT for an hour to obtain the MR ionogels A₆₀, A₁₂₀ and A₂₄₀, MR ionogels B₆₀, B₁₂₀ and B₂₄₀, MR ionogels C₆₀, C₁₂₀ and C₂₄₀, respectively.

Figure 2 presents the results of steady shear experiment on MR ionogels A, B and C generated at different densities of magnetic flux. The shear stress curves ascended as the magnetic field increased until reaching saturation at relatively higher magnetic field strength, where the shear stress curves nearly overlapped. It was also observed that the MR ionogel samples with higher polymer fractions exhibited more pronounced shear stress difference at various magnetic fields.

Besides, FigureS3-5 demonstrated the magnetic field dependent shear stress of the MR ionogels samples under a kept strain, which would be helpful for understanding the MR behavior.



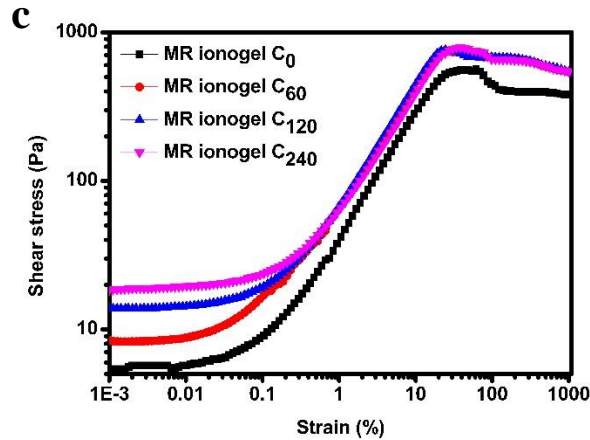


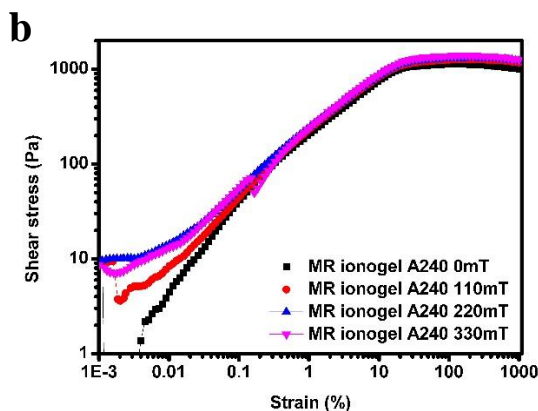
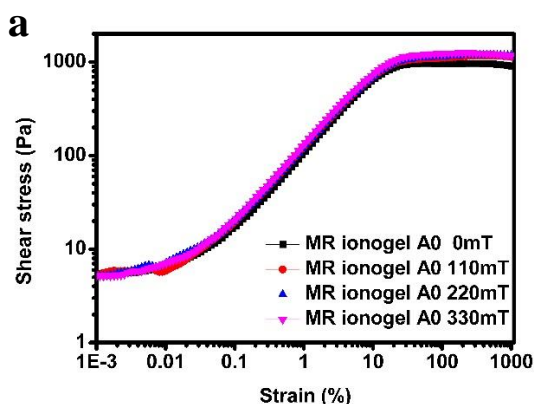
Figure 2. Rheological properties of MR ionogel fabricated at various magnetic field during photo-initiation process (a) MR ionogel A, (b) MR ionogel B, (c) MR ionogel C.

The rheological behavior of these MR ionogel samples and the effect from the magnetic field may be explained by the permanent formation of dipolar magnetic nanoparticles in the fabrication process. When no magnetic field is applied, the magnetic nanoparticles distribute randomly in the ionogel network scaffold, contributing minimum variation to the overall mechanical properties. Under an applied external magnetic field, the magnetic nanoparticles acquire magnetic moment that competes against the thermal fluctuation interacting with the base ionogel matrix, which results in the directionally ordered alignments. As the strength of external magnetic field increases, the involvement of magnetic nanoparticles in the field-induced structure increases as well. As a result, the shear stress reaches a maximum value. The increased stress difference with respect to the increased polymer content can be attributed to the increased resistance of polymer network against the magnetic force, leading to delay in shear stress saturation. The affinity to the internal structural variation and rheological properties ensures customizable property of the proposed MR ionogel.

Beside the significant manipulation of the physical properties of MR ionogel, the established orderly alignments of silica coated iron oxide nanoparticles also give a new feature to these MR

ionogels, MR effect, where magnetic nanoparticles bind more closely with each other under escalating external magnetic field, and more force is required to twist or deform them.

As presented in Figure 3a–f, the MR effect can be evidenced by the steady shear results of isotropic MR ionogels A₀, B₀, and C₀ (MR ionogel samples fabricated without magnetic field) and anisotropic MR ionogels A₂₄₀, B₂₄₀, and C₂₄₀ (MR ionogel samples fabricated under a magnetic field of 240 mT) upon incremental external magnetic field. The MR effect could be evaluated by the scaling parameter as defined by the ratio of initial shear stress under maximum external magnetic field to that under zero-field. The scaling parameter value increased from 1.08 to 2.45 for MR ionogel A₀ and A₂₄₀, 5.84 to 7.77 for MR ionogel B₀ and B₂₄₀, 8.87 to 9.29 for MR ionogel C₀ and C₂₄₀. It is larger for the anisotropic samples than those for the isotropic samples. Moreover, the ionogel with higher content of polymer demonstrates a more pronounced MR effect. **The corresponding dynamic rheological test results are presented in FigureS6-11 of supporting information.**



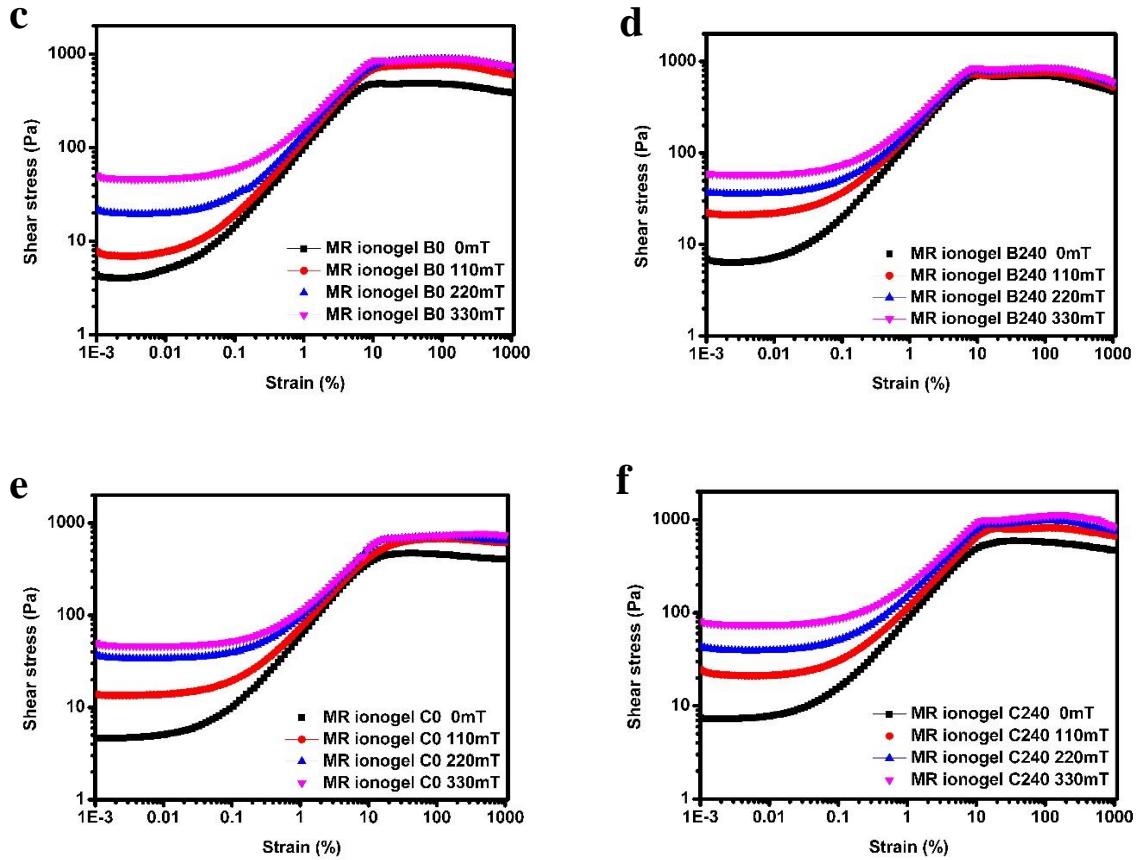


Figure 3. Rheological properties of MR ionogel a, c and e) Isotropic MR ionogel samples A₀, B₀ and C₀ (MR ionogel samples that possess random magnetic nanoparticle distribution) and b, d, f) Anisotropic MR ionogel samples A₂₄₀, B₂₄₀ and C₂₄₀ (MR ionogel samples that possess oriented magnetic nanoparticle alignment) with respect to external magnetic field.

The ascending trend of the scaling parameter for anisotropic MR ionogel samples occurs because the orderly alignments lead to a maximum resistance to external deformation, while the random orientation of magnetic particles in isotropic MR ionogel samples leads to some cancellation effects that weakens the effect of magnetic field. Moreover, the more pronounced MR effect with respect to an increased amount of polymer shows that MR ionogels based on a softer and more flexible ionogel matrix exhibit a better adoption of the magnetic particle structures within the

softer and more flexible ionogel based matrix network, and a conformed result to the results shown in Figure 2a-c.

The conductivity of MR ionogel is calculated according to Equation 1, and is estimated from the Nyquist plots (Figure 4a-f)

$$\alpha = L/AR_c \quad (1)$$

where α is the ionic conductivity of the MR ionogel in mS/cm, L is the thickness of the ionogel in cm, A is the area of the ionogel in cm², and R_c is the bulk resistance (Ω) obtained from the first intercept on the x-axis of the impedance data in the complex plane.

Sample	Conductivity (mS/cm)	Sample	Conductivity (mS/cm)	Sample	Conductivity (mS/cm)
A ₀	3.78	B ₀	3.31	C ₀	2.23
A ₆₀	3.98	B ₆₀	3.47	C ₆₀	2.35
A ₁₂₀	4.12	B ₁₂₀	3.60	C ₁₂₀	2.99
A ₂₄₀	4.22	B ₂₄₀	3.96	C ₂₄₀	3.43
Ionogel A	4.3	Ionogel B	4.04	Ionogel C	3.56

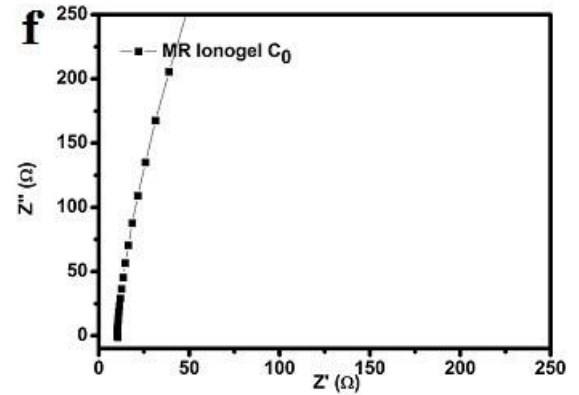
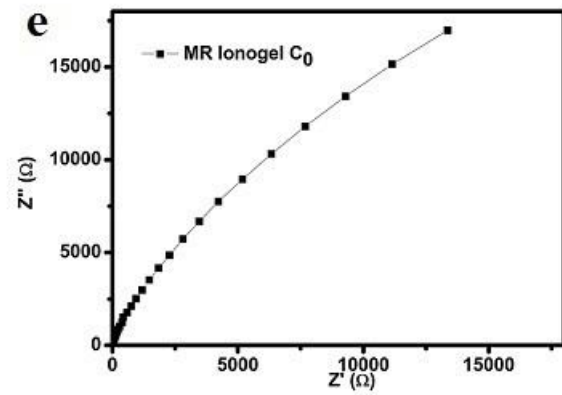
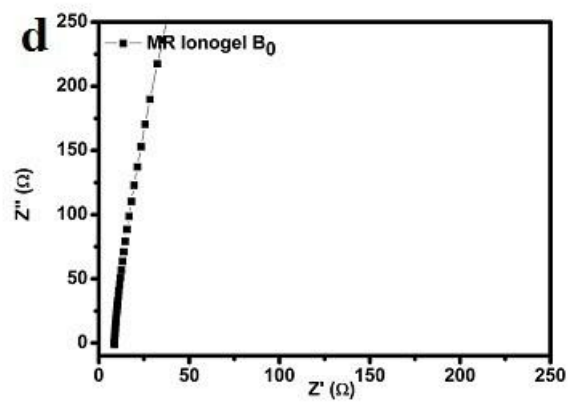
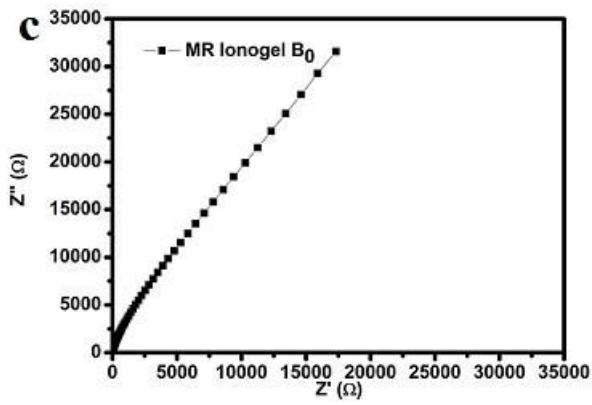
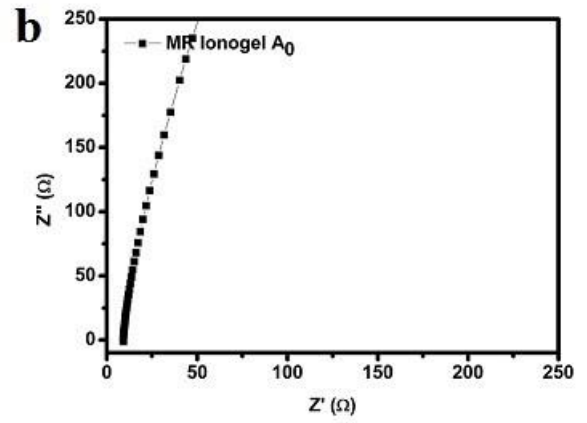
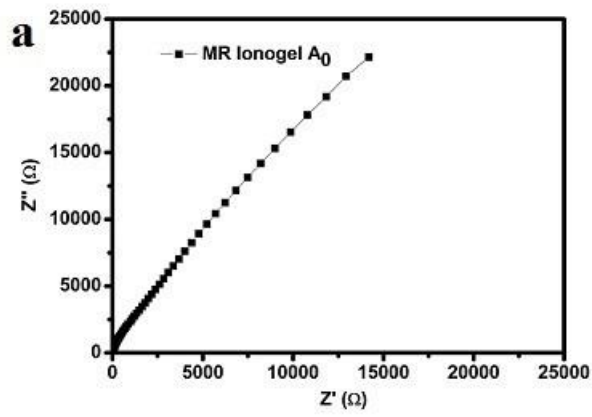
Table 1. The ionic conductivity of MR ionogel and neat ionogel matrix samples

The ionic conductivity for all these MR ionogel samples is summarized in Table 1 with the conductivity of neat ionogel matrix material listed as comparison. The conductivity for MR ionogel A, B, C increased from 3.78, 3.31 and 2.23 mS/cm to 4.22, 3.96 and 3.43 mS/cm with the increased magnetic field from 0 to 240 mT at fabrication, respectively. Such a trend is similar to the shear stress evolution with respect to external magnetic field derived from the rheological

experiments. The conductivity of the ionogel is also affected by the content of PEO. The ionogel with higher amount of non-conductive PEO exhibits lower ionic conductivity under the same fabrication magnetic field. The samples without PEO (sample A) show higher ionic conductivity than sample B (1 wt% PEO) and C (3 wt% PEO). **Moreover, with the fabricating magnetic field strength getting higher, the conductivity of MR ionogel samples were approaching and comparable to the conductivity of original ionogel matrix materials, which showed that the field-induced microstructure would not undermine the electrical capability of original ionogel matrix materials, once it was completely established.**

The increase in ionic conductivity with increase in magnetic field establishes the interdependency between conductivity and dipolar magnetic alignment in these MR ionogel samples. When a curing magnetic field is not applied or at small amplitude, there exists a similarity between the directional magnetic force leading to an orderly alignment and a thermal force favoring a random orientation of magnetic particles. Consequently, most magnetic particles end up drifting in the ionogel matrix. Such randomness in the microstructure hinders the charge carriers transporting and reduces the conductivity [34]. As the magnetic field increases, the magnetic force gradually regulates the orientation of magnetic particles during the fabrication process and more magnetic particles are incorporated into the orderly alignments forming a smoother pathway for charge carriers' transport, which results in an increase in conductivity [26]. When the external magnetic field is large enough, all the magnetic particles are adopted in alignments and conductivity reaches saturation. The delayed saturation in conductivity with respect to increasing PEO content may be attributed to the increased resistance of polymer network competing against the magnetic force that slows down the process of alignment formation. The field controllable conductivity of MR ionogel, is in accordance with its

mechanical evolution at the external magnetic field. This unique feature not only allows us to conveniently customize the conductivity of MR ionogel for specific applications, but also suggests a feasible method of generating electrolyte with simultaneously improved mechanical strength. A diagram is provided in Figure 4g, which illustrate the mechanism of enhancing the mechanical properties and conductivity of MR ionogels.



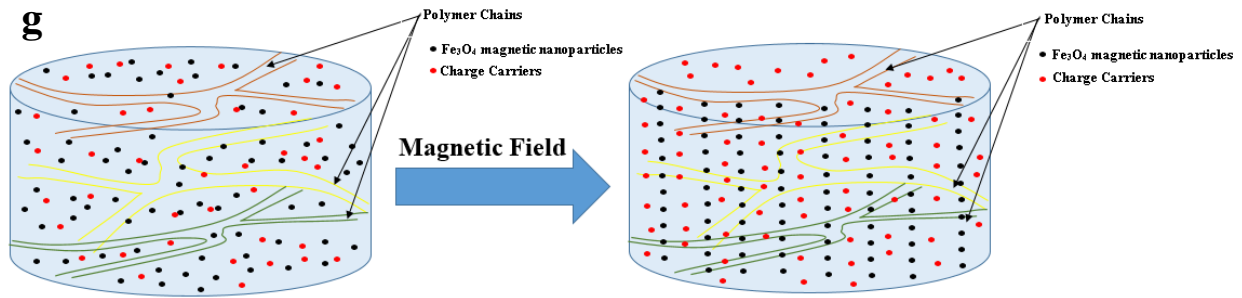


Figure 4. Nyquist plots of (a) Isotropic MR ionogel A_0 . (c) Isotropic MR ionogel B_0 . (e) Isotropic MR ionogel C_0 and corresponding expanded views b, d and f). (g) Diagram which illustrate the mechanism of structure formation of MR ionogel with the application of magnetic field.

Microscopic observation of the structural differences between the MR ionogels (Figure 5) provides direct evidence to explain their physical properties. There is a random distribution of magnetic particles in the isotropic MR ionogel, and an orderly alignment in the anisotropic MR ionogel. The orderly alignments, as proved by the rheological and conductivity experiments, would be expected to lead to simultaneous improvement in mechanical modulus and conductivity.

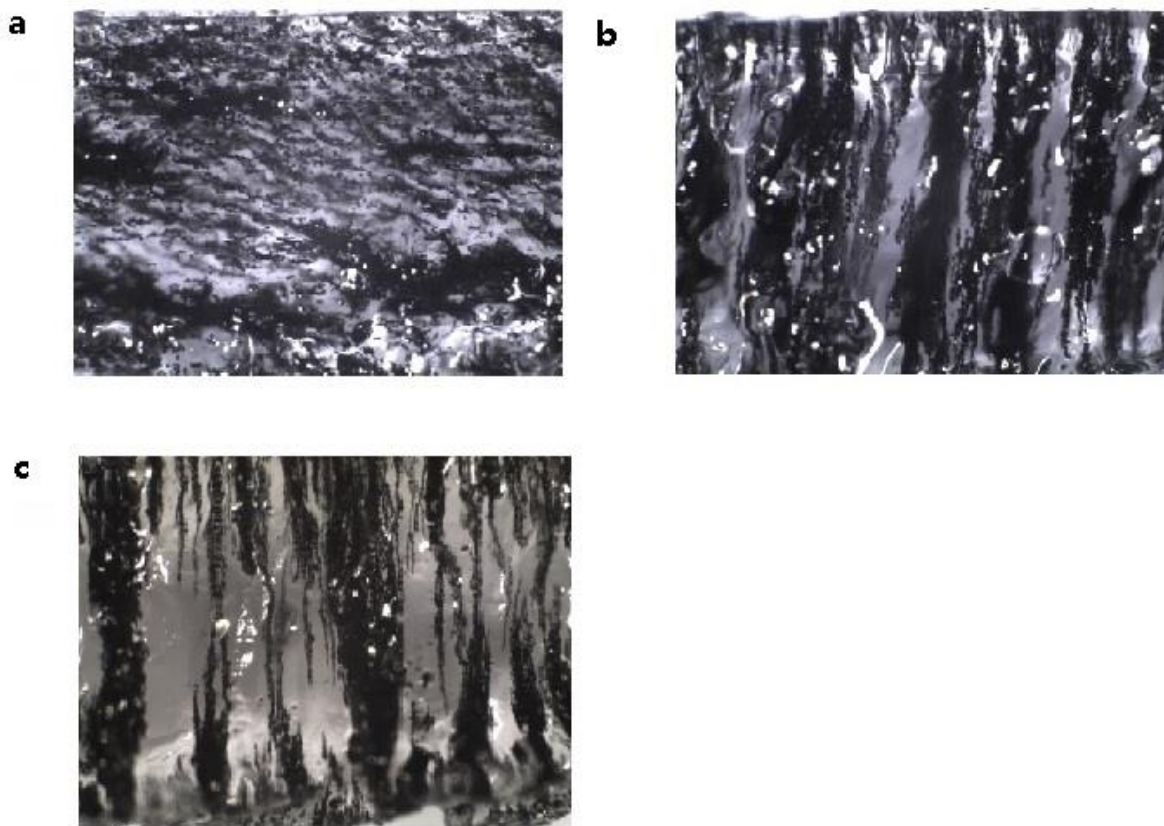


Figure 5. Microscopic observation ($\times 200$ magnification) of MR ionogel samples (a) A_0 , (b) A_{120} and (c) A_{240}

The conductivity test was also repeated under an external magnetic field of 100mT. A similar conductivity was obtained as that without magnetic field (Table S2), which ensures that the MR ionogel could still function properly as an electrolyte upon application of a magnetic field.

Till now, it has been clearly demonstrated that the mechanical properties and ionic conductivity of MR ionogels define affinity to an external magnetic field. The potential application of such solid electrolyte material was studied in supercapacitors.

Cyclic voltammograms (CVs) of the supercapacitors, using MR ionogel electrolyte and commercial active carbon electrodes, generated at different magnetic fields (0 mT, 150 mT and 300 mT) with and without an external magnetic field at a scan rate of 50 mV/s are shown in

Figure 6a–c. When a magnetic field was not applied, all the supercapacitors showed a nearly rectangular CV curve (black line) in the voltage range of 0-3 V, indicating a nearly ideal capacitive behavior. Such performance could be attributed to the good ionic conductivity of the ionogel electrolyte. When an external magnetic field was applied, no obvious shape change of CV curves can be found (red line). Such stable capacitive performance indicates the stability of ionogel electrolyte upon external magnetic field. These results clearly prove the possibility of applying the MR ionogel samples in the development of flexible electronic devices due to their outstanding operation stability upon magnetic field on-off situation.

The charge/discharge results of MR ionogel based supercapacitors are presented in Figure 6d–f. The charge/discharge curves of our supercapacitor showed nearly symmetrical triangular shapes from 0 to 3V at all the applied current densities, indicative of the good ionic conductivity and stability of the MR ionogel electrolyte. The specific capacitance (C_{sp}) of the device can be calculated in F/g from the discharge curves using Equation 2 [36].

$$C_{sp} = \frac{I \Delta t}{m \cdot \Delta V} \quad (2)$$

where I is the discharge current in A, Δt is the discharge time in s, **and m is the total** mass of the active material (activated carbon) on both electrodes in g, ΔV is the potential window in V.

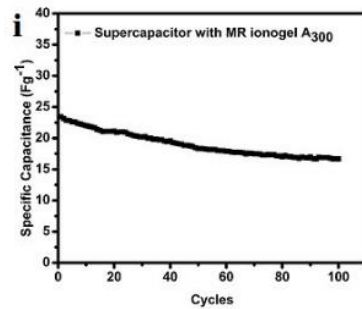
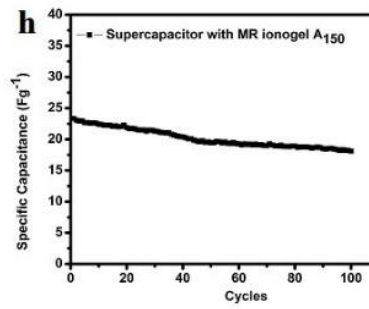
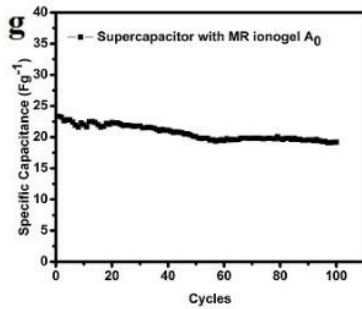
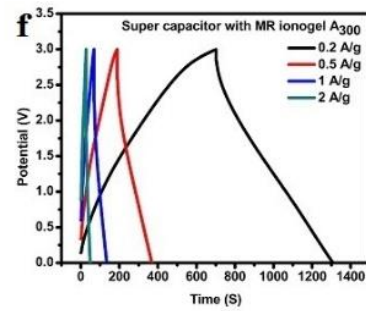
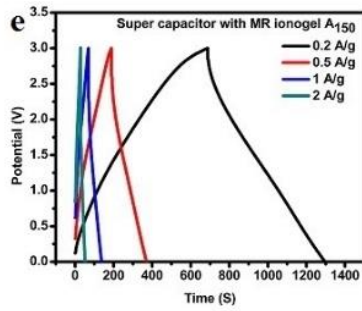
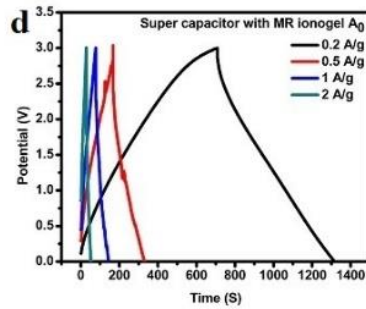
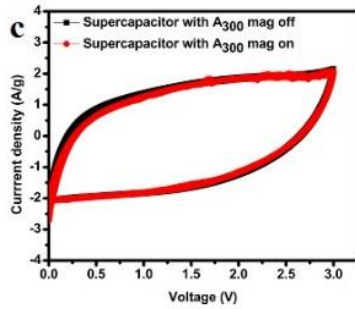
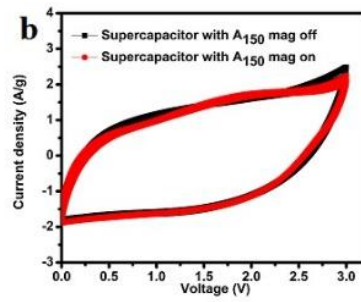
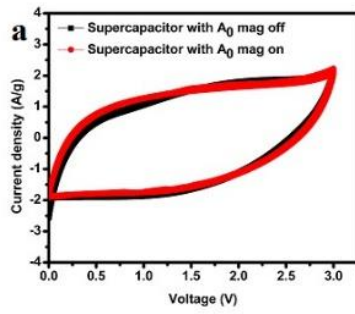


Figure 6. Cyclic voltammograms of supercapacitors with an electrolyte of a) MR ionogel A₀, b) MR ionogel A₁₅₀, c) MR ionogel A₃₀₀ at a scan rate of 50 mV/s from 0-3 V under magnetic field on-off conditions. Charge/discharge performance of supercapacitors with an electrolyte of d) MR ionogel A₀, e) MR ionogel A₁₅₀, f) MR ionogel A₃₀₀ at the current densities of 0.2 A/g, 0.5 A/g, 1 A/g and 2A/g. Cycling stability of supercapacitors with an electrolyte of g) MR ionogel A₀, h) MR ionogel A₁₅₀, i) MR ionogel A₃₀₀ at the current density 1A/g.

The resultant specific capacitance is listed in Table S3. At the same current density, these supercapacitors using MR ionogels fabricated at different magnitudes of magnetic field all show similar C_{sp}, indicating that the improved mechanical modulus of MR ionogels formed at high magnetic field due to the formation of internal alignment did not affect the ionic conductivity. These supercapacitors also show a good rate performance. Taking MR ionogel A₀ as an example, the highest C_{sp} of 40.6 F/g has been delivered at a current density of 0.2 A/g, while it can still deliver a relatively large capacitance of 22.4 F/g at 1 A/g, and 15.4 F/g at 2 A/g. These results may suggest that these MR ionogels could perform reasonably in supercapacitors under fast charge/discharge conditions.

The performance of different supercapacitors over 100 cycles using A₀, A₁₅₀ and A₃₀₀ as an electrolyte at a high current density of 1A/g are shown in Figure 6g–i. A slight decrease of C_{sp} can be observed, from 22.4 to 19.2 F/g for A₀, from 22.9 to 19.1 F/g A₁₅₀ and from 22.3 to 17.7 F/g for A₃₀₀. The corresponding capacitance retention rate is 85.7%, 83.4% and 79.4%, respectively. Such relatively high capacitance retention rate suggests the potential use of MR ionogels as electrolytes in energy storage applications.

4. Conclusions

In summary, a magneto-rheological ionogel (MR ionogel) is developed by building a magnetic field controlled structure in a UV cross-linkable matrix. The planting of structured magnetic nanoparticles in the matrix ensures the formation of a freestanding MR ionogel film with an ultra-high ionic liquid fraction (up to 88 wt%) and sound mechanical properties following the fortifying effect of field induced magnetic microstructure, as well as an obvious MR effect upon a magnetic field. It reveals a feasible way to develop a novel multifunctional ionogel with precisely customized physical properties, which can be applied as solid electrolyte for flexible high performance electronic devices with prominent safety features. Being a mechanically robust elastomeric material, this MR ionogel could also be considered as a novel MR elastomer that significantly broadens the application of this class of smart materials in sensor and actuator research.

Supporting Information

A list of associated content available in a separate document:

Figure S1. VSM and CV test for magnetic nanoparticles with and without silica coatings

Figure S2. Rheological properties of ionogel base matrix

Figure S3-5. Field dependent shear stress of MR ionogel samples under constant strain of 0.1%

Figure S6-11. Dynamic rheological properties of isotropic MR ionogel samples

Table S1. Summary of fabricated ionogel and MR ionogel samples

Table S2. Field-on and field-off conductivity for MR ionogel samples

Table S3 Capacitances of supercapacitors incorporating various MR ionogel samples

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