

# Tough Ionogel-in-Mask Hybrid Gel Electrolytes in Supercapacitors with Durable Pressure and Thermal Tolerances

Dr. Xinhua Liu<sup>[a]</sup>, Dr. Billy Wu<sup>[b]</sup>, Prof. Dr. Nigel Brandon<sup>[c]</sup> and Prof. Dr. Qigang Wang<sup>\*[a]</sup>

**Abstract:** A primary challenge of gel electrolytes in development of flexible and wearable devices is their weak mechanical performances, including their compressive stress, tensile strength, and puncture resistance. Here we prepare an ionogel-mask hybrid gel electrolyte, which successfully achieves synergic advantages of the high mechanical strength of the mask substance and the superior electrochemical and thermal characteristics of the ionogel. The fabricated supercapacitor can maintain a relatively stable capacitive performance even under a high pressure of 3236 kPa. Meanwhile, with the good thermal stability of the composite gel electrolyte, the solid-state supercapacitor can be operated at high temperatures ranging from 25 °C to 200 °C. The ionogel-mask hybrid gel can be superior tough gel electrolyte for solid-state flexible supercapacitors with durable advantages in both high temperatures and pressures.

The development of flexible and wearable energy storage devices has attracted increasing attention for a wide range of applications. Supercapacitors are considered to be one of the most promising choices owing to their long operating lifetimes, high power densities, low environment impact, and intrinsic safety.<sup>[1-6]</sup> The realization of high-performance all-solid-state flexible supercapacitors requires materials with high ionic conductivity and a wide electrochemical window, as well as robust mechanical and thermal stability of their gel electrolytes.<sup>[7-10]</sup> Currently, ionogels with excellent electrochemical performances and thermal stability have been considered as gel electrolytes in all-solid-state supercapacitors.<sup>[11-15]</sup>

However, it is important to highlight that it is impossible for all flexible/wearable devices to avoid mechanical deformation such as compressing, stretching, and bending in fabrication and/or use. The applied pressures, both average and local pressure, may vary with time, temperature and location, and affect the electrochemical performances. Of these, the local pressure can be the main cause of short-circuits in the cell. Meanwhile, the fabricated supercapacitors, which possess dual advantages of mechanical strength and thermal stability, have a great potential to be used in combination with high temperature lithium or sodium batteries in harsh temperature environments. Therefore, there is a need to develop tough ionogel electrolytes with a high puncture resistance at room temperature and high temperatures. To the best of our knowledge, ionogel electrolytes with high puncture strength or high temperature tolerance have not previously been reported. Only a few studies report the tensile strength but with a limited value of about 15-33 kPa.<sup>[16, 17]</sup> Therefore, conventional ionogels, which are prepared mainly by physical mixing or covalent gelation of vinyl polymers, cannot achieve the required mechanical strength.

The supramolecular approach has been proved to be an effective way to prepare tough hydrogels.<sup>[18-20]</sup> In our previous work, we employed a supramolecular approach to prepare tough gel electrolytes with the addition of chitosan which show much higher compressive strength than conventional electrolytes.<sup>[21, 22]</sup> In view of the high porosity and mechanical strength, facial mask

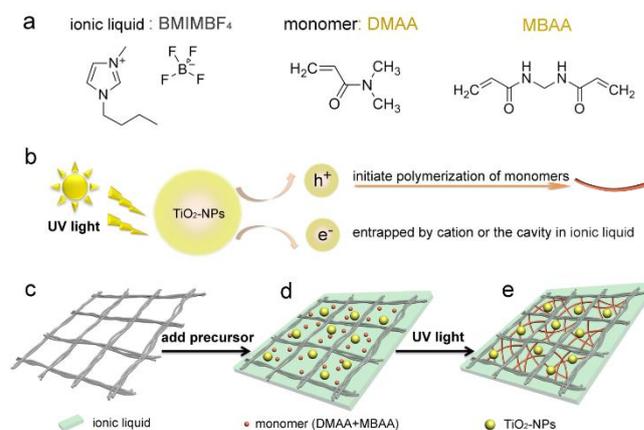


Figure 1. Schematic illustration of the composite ionogel from monomer precursor solution and mask scaffold. a) The molecular structures. b) The mechanism of the TiO<sub>2</sub>-NPs initiated UV polymerization. c) The mask scaffold. d) The mask and added precursor solution. e) The preparation of ionogel-in-mask hybrid gel electrolyte via in situ UV-initiated polymerization.

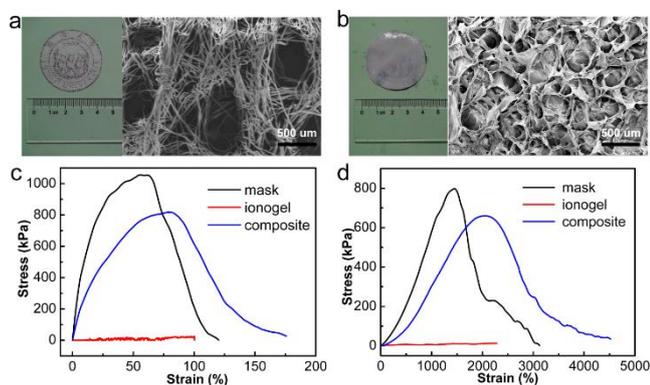
membranes can be an alternative choice in the preparation of hybrid gel electrolytes, with excellent mechanical advantages. As low cost porous scaffolds, the disposable thin film masks have been widely used in beauty treatment and medical applications with combined advantages of good mechanical strength and liquid retention ability, but at the same time, the current waste management of pyrolytic combustion needs high operation cost and causes environmental pollution because of the secondary pollutant during incineration.<sup>[23]</sup> In view of this, we employed an ionogel as the electrolyte via TiO<sub>2</sub> nanoparticles (TiO<sub>2</sub>-NPs, average size: 25 nm) initiated polymerization with a cotton mask as the porous scaffold to prepare an ionogel-in-mask hybrid gel. Here, the cotton mask contains cellulose molecules and many -OH groups which can provide supramolecular effects between the ionogel and the mask scaffold to enhance the mechanical strength of the hybrid gel. The final hybrid gel electrolyte therefore combines the mechanical advantages of the mask and the electrochemical characteristics of the ionogel.

The preparation of the ionogel-in-mask hybrid gel electrolyte can be readily achieved via UV-initiated polymerization. The precursor has the following components: 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>), N, N-dimethylacrylamide (DMAA), methylene-bis-acrylamide (MBAA) and TiO<sub>2</sub> nanoparticles. Their molecular structures are shown in Figure 1a. Firstly, TiO<sub>2</sub>-NPs and DMAA (containing 3 wt% MBAA) are dissolved in BMIMBF<sub>4</sub> to obtain a viscous precursor solution (mass ratio: 0.25: 5: 94.75) via magnetic stirring. Then, the cotton mask was put in the precursor to absorb sufficient liquid (Figure 1d). The mask scaffold possesses a porous structure (Figure 1c) and results in good liquid retention ability. Finally, the ionogel-in-mask hybrid gel electrolyte can be prepared after a 45 min UV-initiated polymerization (with an average intensity of 96 mW/cm<sup>2</sup> at 365 nm). Herein, TiO<sub>2</sub>-NPs were employed not only as the inorganic-photoinitiator for the polymerization but also as the reinforced nanofiller to provide inorganic-crosslinking that can enhance the mechanical strength of the ionogel through the supramolecular effects. Figure 1b shows the mechanism of the TiO<sub>2</sub>-initiated polymerization. Under UV irradiation, TiO<sub>2</sub>-NPs can produce holes (h<sup>+</sup>) and electrons. It is these holes that can serve

as the initiator and react with the monomers. The electrons can be entrapped by the cations or cavity in ionic liquid to form solvated electrons. The signals of chain growth radicals captured by electron paramagnetic resonance (EPR) spectrum can further prove this point (Figure S1, Supporting Information). The time sweep measurement can test the crossover points from the storage modulus ( $G'$ ) and loss modulus ( $G''$ ) which demonstrate the gelation kinetics. (Figure S2, Supporting Information).

In this case, the optimum synthetic condition was considered to be 0.25 wt%  $\text{TiO}_2$ -NPs and 5 wt% monomer. The pure ionogel with 0.25 wt%  $\text{TiO}_2$ -NPs showed a higher level of toughness after undergoing large deformations and still kept good mechanical integrity (Figure S3, Supporting Information). The ionogel with 5 wt% monomers can achieve a Young's modulus value of 2.6 kPa and maintain a high ionic conductivity of  $3.5 \text{ mS cm}^{-1}$  (Figures S4 and S5, Supporting Information). Therefore,  $\text{TiO}_2$ -NPs (with an average size of 25 nm, Figure S6, Supporting Information) can serve as both effective initiators with a final monomer conversion of 92.2% after 45 minutes of UV irradiation (Figure S7, Supporting Information) and inorganic cross-linking points to achieve good mechanical strength.<sup>[24]</sup>

The porous structures of the cotton mask (Figure 2a) can endow the mask with good liquid retention ability (about 600 % by mass). After UV-polymerization, the ionogel and the mask combine into a single structure with a thickness of about 350  $\mu\text{m}$  (Figure 2b and Figure S8, Supporting Information). The obtained ionogel-in-mask hybrid gel electrolyte successfully combines the mechanical strength of the mask with the ionic conductivity of the ionogel. Figure 2c shows the tensile stress-strain curves for ionogel, mask and their composite, where it is possible to notice the hybrid gel possesses extreme elongation prior to failure. Although the ionogel has lower tensile strength (21 kPa), this gap can be successfully filled by adding the mask scaffold. The addition of the mask significantly improves the tensile strength of the ionogel-in-mask hybrid gel electrolyte (854 kPa) by the close connection between the ionogel and mask. Meanwhile, the puncture tolerance is a critical factor in resisting short-circuits during use. Herein, we propose the importance of puncture resistance and provide an effective approach to measure the compressive tolerance of the gel electrolyte and improve the reliability of the device. As shown in Figure 2d, the mask scaffold can achieve an excellent puncture stress value of 798 kPa but with a failure strain of 1,532%. Instead, the ionogel can reach a higher strain of 2,283% but maintains a very low puncture value of 13 kPa. On this basis, the ionogel-in-mask hybrid gel electrolyte can combine the puncture resistance of the mask and



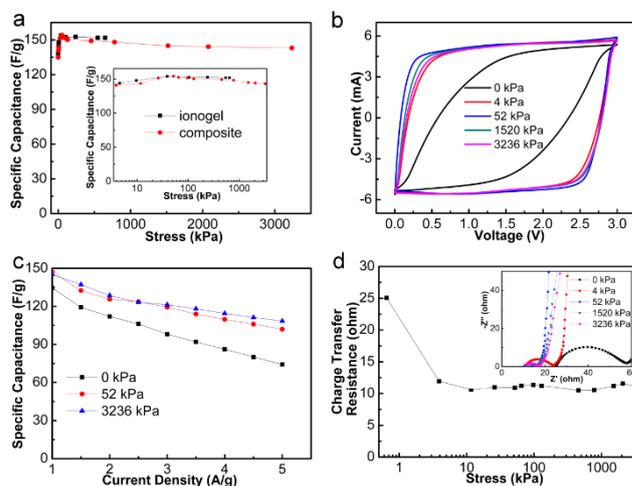
**Figure 2.** Photographs and SEM images of a) the mask scaffold and b) the free-standing ionogel-in-mask hybrid film. c) Tensile stress-strain response of mask, ionogel and mask-in-ionogel hybrid gel. d) Puncture stress-strain curves of mask, ionogel and mask-in-ionogel composite.

the strain flexibility of the ionogel, maintaining a high combined puncture strength of 661 kPa after applying large strains of 2,130%. The significant mechanical improvement can be

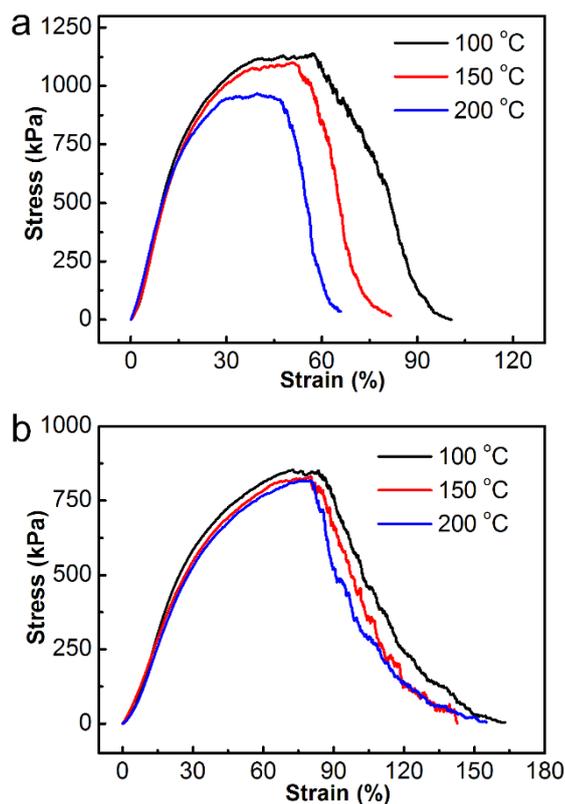
attributed to the addition of cotton mask which contains a major component of cellulose (over 90%) thus can provide supramolecular effects via the existing  $-\text{OH}$ .<sup>[25]</sup>

These excellent mechanical properties endow the ionogel-in-mask hybrid gel electrolyte with high mechanical tolerance in all-solid supercapacitor fabrication, ensuring stable capacitive performance whilst applying various stresses. For comparison, we employed commercial activated carbon (YP 80F, 2100  $\text{m}^2/\text{g}$ ) as the electrode material for the supercapacitor construction. Compared to the pure ionogel-based supercapacitor, the hybrid gel electrolyte based device can achieve similar specific capacitance values when applying lower stresses (Figure 3a). In particular, the hybrid gel based supercapacitor can maintain a relatively stable specific capacitance ( $C_{\text{sp}}$ ) value even when applying much higher stresses than the pure ionogel because of the mechanical properties of the added mask scaffold.

As shown in Figure 3a, the capacitance increases with increasing pressure, levelling off at a pressure of approximately 52 kPa. The enhanced capacitive performance can be further proved by the cyclic voltammetry (CV) curves in Figure 3b which shows rectangular curves when applying high stresses. Further increases in the stress causes lower ionic conductivity and a resulting decrease in capacitive behaviors because of the closed pores of the gel electrolyte under higher pressures (Figure S9, Supporting Information). In this process the effect of pressure is the dominant factor, discussed further below. It is further shown in Figure 3c, that the performance of the ionogel-in-mask hybrid based supercapacitor, when applying higher compressive load (52 kPa and 3236 kPa), maintained a higher specific capacitance value than the device without applied pressure. The source of this improved performance can be seen in Figure 3d which shows the impedance spectra of the ionogel-in-mask supercapacitor. Here, it is evident that a combination of a reduction in the series resistance and charge transfer resistance gives rise to the improved performance. The cause of this can be explained by two mechanisms.<sup>[26, 27]</sup> An increase in pressure can decrease contact



**Figure 3.** a) The comparison of specific capacitance values between the pure ionogel and ionogel-in-mask composite based supercapacitors calculated from charging-discharging processes at the current density of 1 A/g as a function of compressive stress b) CV curves of the ionogel-in-mask hybrid gel electrolyte based all-solid-state supercapacitor under compressive stresses of 0 to 3236 kPa. c) The correlation of specific capacitance with current density under under compressive stresses of 0 kPa, 52 kPa, and 3236 kPa. d) Variation of the charge-transfer resistance of the supercapacitors under compressive stresses of 0 to 3236 kPa.

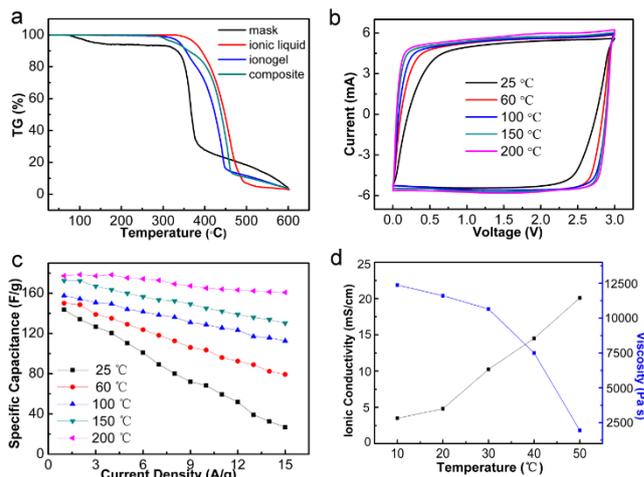


**Figure 4.** Tensile stress-strain response of a) mask and b) hybrid gel applying various high temperatures.

resistance between current collectors and the electrode material, as well as decrease the diffusion distance of ions in the electrolyte resulting in a decreased series resistance. The lower charge transfer resistance is likely due to the thinner electrodes with greater surface area per unit volume when under compression, which yields a higher electrode utilisation and /or active area, as the region of highest current density is typically at the electrode-separator interface.

In addition to the mechanical toughness when applying compressive stresses at room temperature, the hybrid gel can maintain high mechanical strength even at high temperatures. Figure 4a shows the tensile strength of the cotton mask after 2h heat treatment at 100 °C, 150 °C and 200 °C. The tensile strength of the pure cotton mask keeps high mechanical strength at 100 °C but decreases applying high temperatures of 150 °C and 200 °C (Figure S10a, Supporting Information). Figure S11(Supporting Information) also shows the yellow colour at high temperatures indicating the possible fibre carbonization. On the contrary, the hybrid gel remains the same colour and tensile strength applying various high temperatures (Figure S12, Supporting Information). Therefore, the hybrid gel possesses excellent mechanical strength at high temperatures which should be attributed to the protection of the thermal stable ionogel (Figure 4b and Figure S10b, Supporting Information). Through our novel approach of mask-in-ionogel composite, we report a reduced tensile strength of 2% at 200 °C while the pure cotton mask shows a 26% decrease in tensile strength.

Figure 5a shows the thermal stabilities of the ionic liquid, mask, ionogel and their composite. It is worth mentioning that the ionogel-in-mask composite possesses a high thermal stability as demonstrated by the low mass loss regimes up to an operating temperature of 270 °C in the thermal gravimetric trace (TGA). In view of this thermal stability, the ionogel-in-mask hybrid gel electrolyte based supercapacitor was further tested at temperatures up to 200 °C. (the assembly pressure was about 3 kPa ). As shown in Figure 5b, the cyclic voltammetry curves



**Figure 5.** a) TGA curves of the mask, BMIMBF<sub>4</sub>, ionogel, and ionogel-in-mask composite. b) CV-curves of the all-solid supercapacitor applying ionogel-in-mask hybrid gel electrolyte at a scan rate of 20 mV/s and temperatures of 25 °C to 200 °C. c) Variation of C<sub>sp</sub> with current density at temperatures of 25 °C to 200 °C. d) The effect of temperature of ionic conductivity and viscosity of the ionogel-in-mask hybrid gel electrolyte.

become increasing rectangular as the temperature increases from 25 °C to 200 °C. Figure 5c presents the specific capacitance at various current densities operated at different temperatures. The C<sub>sp</sub> value of 177 F/g at 200 °C is higher than that of 143 F/g at 25 °C at a low current density of 1 A/g. With the temperature increasing from 25 °C to 200 °C, the maintained C<sub>sp</sub> gap becomes more obvious at higher current densities, where the ionic conductivity begins to become the rate limiting factor. It is notable that the maintained C<sub>sp</sub> value at 200 °C (160 F/g) is about six times the value determined at 25 °C (26 F/g) at a higher current density of 15 A/g. The enhanced electrochemical performance could be attributed to the increased amount of charged ions which can access both within the gel matrix and through the electrode-electrolyte interfaces. Higher temperature can accelerate ion migration and diffusion to the inner pores of the activated carbon, resulting in an increase in pore filling efficiency of the ions, leading to higher specific capacitances.

Figure 5d supports this explanation. When the temperature increased from 25 °C to 200 °C, the ionic conductivity increased from 3.5 mS cm<sup>-1</sup> to 20.1 mS cm<sup>-1</sup> while the viscosity decreased from 12,377 Pa.s to 1,943 Pa.s. As presented in the literature,<sup>[28]</sup> the ion mobility ( $\mu$ ) is inversely related to the viscosity ( $\eta$ ) of the electrolyte as  $\mu = q/6\pi r\eta$  ( $q$  is the electronic charge on each charge carrier;  $r$  is the effective hydrodynamic radius). The conductivity ( $\sigma$ ) of an electrolyte can be given by  $\sigma = nq\mu$  and depends upon the carrier concentration ( $n$ ) and ion mobility. Therefore, it is logical to infer that the accelerated ion diffusion rate within the gel electrolyte with lower viscosity results in enhanced ionic conductivity at higher temperatures. Furthermore, the contact resistance at the interface between the gel electrolyte and activated carbon decreases with increasing temperature (Figure S13, Supporting Information). Taken together, the swollen conducting pathways within the hybrid gel matrix with increased temperature can result in more effective contact, and accelerate the movements of charged ions and polymer chains, thus enhancing the electrochemical performance.

Furthermore, the robust gel electrolyte endows the fabricated supercapacitor with good flexibility. As shown in Figure S14 (Supporting Information), there is only a slight difference in the CV curves under various degrees of bending (0°, 30°, 60° and 90°) applying a stress of 3 kPa, indicating that the hybrid gel electrolyte can be used in solid-state flexible supercapacitors with good mechanical strength, flexibility and stability. Moreover, the hybrid

gel electrolyte based supercapacitors possess robust cycling stability when applying various stresses and high temperatures (Figure S15, Supporting Information). We anticipate that the ionogel-in-mask hybrid gel can be used as a robust gel electrolyte for all-solid-state flexible supercapacitors with durable advantages in both high pressure and temperature applications. In conclusion, it has been demonstrated that ionogel-in-mask gel electrolytes can be prepared by UV initiated polymerization which can be used as suitable electrolytes and separators for solid-state supercapacitors with compressive and thermal tolerance. This is a promising approach to prepare robust hybrid gel electrolytes by combining an ionic conducting gel within tough porous scaffolds. The hybrid gels have a great potential as mechanically tough gel electrolytes for the fabrication of flexible and wearable devices which have high demands for mechanical properties. Meanwhile, the fabricated supercapacitors possess the dual advantages of mechanical strength and thermal stability, which enable operation in harsh environments. This work also highlights the electrochemical performance changes of supercapacitors under compression and high temperatures, and suggests mechanisms for the observed behaviour, which is rarely reported in the literature, yet is highly relevant to the integration of supercapacitor into energy storage systems.

## Experimental Section

**Preparation of hybrid gel electrolytes:** Typically, TiO<sub>2</sub>-NPs, DMAA (containing 3 wt% MBAA) and BMIMBF<sub>4</sub> were mixed together by the mass ratio of 0.25: 5: 94.75 to obtain a viscous precursor solution through magnetic stirring. Afterwards, the mask was put in the precursor to absorb sufficient precursor solution (about 600% by mass). The preparation of ionogel-in-mask hybrid gel electrolyte can be realised by 45 min UV light polymerization (average 96 mw/cm<sup>2</sup> intensity at 365 nm).

**Characterizations:** The EPR results were obtained by EPR Spectrometer (A300, Bruker). The SEM images of freeze-dried samples were obtained under scanning electron microscope (Hitachi S-4800, JEOL, Japan). The compressive, stretchable, and puncture strengths of ionogels, mask scaffold, and resulting hybrid gels were performed by a tensile-compressive tester (FR-108B, Farui Co.). The thermal stability of ionogels was operated using a Netzsch Simultaneous Thermal Analyzer STA409-PC (Netzsch, Germany). The cyclic voltammetry, impedance measurements, and chronopotentiometry were measured by a Metrohm Autolab PGSTA302N potentiostats-galvanostats (The Netherlands). The storage modulus (G') and loss modulus (G'') were monitored by a Haake RS6000 rheometer (Germany). The intrinsic viscosity of ionogel applying various temperatures was carried out with TA instruments rheometer (ARES; New Castle, DE, USA).

## Acknowledgements

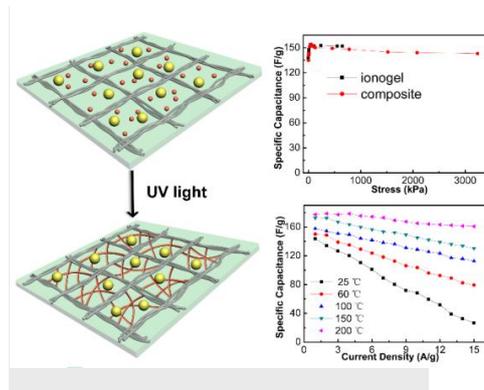
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**Keywords:** gel electrolyte • free-radical polymerization • mechanical strength • thermal tolerance • supercapacitors

- [1] P. Simon and Y. Gogotsi, *Nat. Mater.*, **2008**, *7*, 845-854.  
 [2] J. Wang, X. Li, Y. Zi, S. Wang, Z. Li, L. Zheng, F. Yi, S. Li and Z. L. Wang, *Adv. Mater.*, **2015**, *27*, 4830-4836.  
 [3] J. Zheng, Y. Liu, G. Ji, P. Zhang, X. Cao, B. Wang, C. Zhang, X. Zhou, Y. Zhu, and D. Shi. *ACS Appl Mater Inter*, **2015**, *7*, 23431-23438.

- [4] Y. Yu, C. Yan, L. Gu, X. Lang, K. Tang, L. Zhang, Y. Hou, Z. Wang, M. Chen, O. G. Schmidt, J. Maier, *Adv. Energy Mater.*, **2013**, *3*, 281-285.  
 [5] X. Chen, H. Lin, P. Chen, G. Guan, J. Deng and H. Peng, *Adv. Mater.*, **2014**, *26*, 4444-4449.  
 [6] G. Yu, X. Xie, L. Pan, Z. Bao and Y. Cui, *Nano Energy*, **2013**, *2*, 213-234.  
 [7] J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. Liu and Z. L. Wang, *Angew. Chem. Int. Ed.*, **2011**, *50*, 1683-1687.  
 [8] L. Li, H. Lu, Z. Yang, L. Tong, Y. Bando, and D. Golberg, *Adv. Mater.*, **2013**, *25*, 1109-1113.  
 [9] X. Sun, W. Si, L. Xi, B. Liu, X. Liu, C. Yan, and O. G. Schmidt, *ChemElectroChem*, **2015**, *2*, 737-742.  
 [10] Z. Zhang, X. Chen, P. Chen, G. Guan, L. Qiu, H. Lin, Z. Yang, W. Bai, Y. Luo and H. Peng, *Adv. Mater.*, **2014**, *26*, 466-470.  
 [11] X. Liu, Z. Wen, D. Wu, H. Wang, J. Yang and Q. Wang, *J. Mater. Chem. A*, **2014**, *2*, 11569-11573.  
 [12] M. Beidaghi and Y. Gogotsi, *Energy Environ. Sci.*, **2014**, *7*, 867-884.  
 [13] X. Liu, B. Wang, Z. Jin, H. Wang and Q. Wang, *J. Mater. Chem. A*, **2015**, *3*, 15408-15412.  
 [14] M. F. El-Kady and R. B. Kaner, *Nat. Commun.*, **2013**, *4*, 1475.  
 [15] A. I. Horowitz and M. J. Panzer, *Angew. Chem. Int. Ed.*, **2014**, *53*, 9780-9783.  
 [16] B. Chen, J. J. Lu, C. H. Yang, J. H. Yang, J. Zhou, Y. M. Chen and Z. Suo, *ACS Appl. Mater. Interfaces*, **2014**, *6*, 7840-7845.  
 [17] Y. Kitazawa, T. Ueki, K. Niitsuma, S. Imaizumi, T. P. Lodge and M. Watanabe, *Soft Matter*, **2012**, *8*, 8067-8074.  
 [18] G. Yu, K. Jie and F. Huang, *Chem. Rev.*, **2015**, *115*, 7240-7303.  
 [19] Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara and T. Aida, *Nature*, **2010**, *463*, 339-343.  
 [20] B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.*, **2012**, *41*, 1621-1636.  
 [21] X. Liu, D. Wu, H. Wang and Q. Wang, *Adv. Mater.*, **2014**, *26*, 4370-4375.  
 [22] X. Liu, B. He, Z. Wang, H. Tang, T. Su and Q. Wang, *Sci. Rep.*, **2014**, *4*, 6673.  
 [23] M. Tsakona, E. Anagnostopoulou and E. Gidarakos, *Waste Manage.*, **2007**, *27*, 912-920.  
 [24] C. Liao, Q. Wu, T. Su, D. Zhang, Q. Wu, and Q. Wang, *ACS Appl. Mater. Interfaces*, **2014**, *3*, 1356-1360.  
 [25] A. C. O'SULLIVAN, *Cellulose*, **1997**, *4*, 173-207.  
 [26] C. Masarapu, L. P. Wang, X. Li and B. Wei, *Adv. Energy Mater.*, **2012**, *2*, 546-552.  
 [27] M. W. Verbrugge and P. Liu, *J. Electrochem. Soc.*, **2005**, *152*, D79-D87.  
 [28] M. P. Scott, M. Rahman and C. S. Brazel, *Eur. Polym. J.*, **2003**, *39*, 1947-1953.

The preparation of ionogel-in-mask hybrid electrolytes with synergistic advantages via  $\text{TiO}_2$  initiated UV polymerization is described, which provides a broad approach to prepare porous scaffold based highly tough ionogel electrolytes with durable high pressure and thermal tolerances in supercapacitors.



Xinhua Liu, Billy Wu, Nigel Brandon, and Qigang Wang\*

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