DOI: 10.1002/cnma.201500093

Dye-Sensitized Solar Cells | Very Important Paper |

Stable Hydrophobic Ionic Liquid Gel Electrolyte for Stretchable Fiber-Shaped Dye-Sensitized Solar Cell

Houpu Li,[a] Jiajie Guo,[a] Hao Sun,[a] Xin Fang,[a] Donghai Wang,[b] and Huisheng Peng*[a]

Abstract: Fiber-shaped dye-sensitized solar cells have attracted increasing interest in powering wearable and portable electronic devices. However, the use of liquid electrolytes gives rise to vulnerabilities, greatly limiting their practical applications. Here we develop a stable gel electrolyte based on polymer–ionic liquid gel with high nonvolatility and durability. The gel electrolyte maintains a quasi-solid state from room temperature to 98 °C and can sustain high temperatures up to 300 °C. Based on this gel electrolyte, the resulting fiber-shaped dye-sensitized solar cell achieves a power conversion efficiency of 5.47% that remains at 90% after 30 days. The gel electrolyte makes the device more environmentally adaptive and compatible to bending and stretching deformations.

With the rapid development in modern electronics, portable and wearable devices attract more and more attention in our life. Yet it remains challenging to power them as the current power systems appear in planar or bulky structures that are incompatible with the required weaveability. A new family of fiber-shaped energy harvesting and storage devices have been recently created to solve this problem.[1] For instance, fiber-shaped dye-sensitized solar cells (DSSCs) have been widely studied to produce high power conversion efficiencies up to 8.45%.[2] However, the use of liquid electrolytes brings several drawbacks, including the toxicity and inflammability of organic solvents and the leakage and vaporization of liquid electrolytes with the decay of power conversion efficiencies.[3] On one hand, many efforts have been devoted to explore ionic liquids (ILs), which are nonvolatile and avoid vaporization, but still suffer from the problem of leakage.[3,4] On the other hand, gel electrolytes employing solvents with high boiling points such as 3-methoxypropionitrile (MPN) have been studied due to a deformable structure with no fluidity,[5] avoiding leakage as well as making them promising candidates for flexible devices.[6] However, the vaporization problem which is detrimental for practical applications still remains due to the volatile nature of organic solvents.[7] Furthermore, the hygroscopicity of nitrile or other solvents used in gel electrolytes would also shorten the lifetime of DSSCs.[8] Replacing the organic solvents by solid-state electrolytes such as IL crystals can sufficiently avoid the leakage and vaporization problem,[9] and the hydrophobic nature of plastic crystals also provides resistance to water,[10] but the largely decreased current carrier mobility generally lowers the power conversion efficiencies of DSSCs.[11] In addition, the hardness of IL crystals sacrifices the flexibility and stretchability of the resulting devices, which is disadvantageous for wearable and portable applications.

Herein, a novel gel electrolyte is developed from polymer and hydrophobic ionic liquid to fabricate stretchable fiber-shaped DSSCs. Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) copolymer has been chosen to be the gelata in this electrolyte to produce high stability and gelling performance.[12] 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (BMITFSI), a hydrophobic ionic liquid also with high stability that has been widely used in lithium-ion batteries[13] serves as the main component to offer ionic conductivity (Figure 1 a). Combining the advantages of these two components, the designed electrolyte demonstrates a high stability that overcomes the problems of vaporization and leakage and offers a good contact between the electrolyte and electrode under deformation. The resulting DSSCs based on this gel electrolyte exhibit high stability over time, temperature, moisture, and deformation, which are attributed to the stability of BMITFSI.

The IL gel electrolyte was designed based on the recipe of widely used MPN gel electrolyte, which utilizes PVDF-HFP as gelata and MPN as solvent (Figure S1 in the Supporting Information).[6,12] The crystalline PVDF segments in PVDF-HFP copolymer perform as physical cross linkers to overcome the fluidity and leakage problems, and soft HFP segments provide high strength, flexibility, and electrolyte-containing capacity (Figure 1 b, and Video S1).[14] By replacing the volatile, inflammable, and hydrophilic MPN with nonvolatile, chemically stable, and hydrophobic ionic liquid BMITFSI, the IL gel electrolyte demonstrates much improved stability. The performance of the obtained IL gel electrolyte was compared with the most widely used liquid electrolyte based on acetonitrile (commercial DHS-

[a] H. Li, J. Guo, H. Sun, X. Fang, Prof. H. Peng
State Key Laboratory of Molecular Engineering of Polymers
Department of Macromolecular Science and
Laboratory of Advanced Materials
Fudan University
Shanghai 200438 (China)
E-mail: penghs@fudan.edu.cn

[b] Prof. D. Wang
Department of Mechanical and Nuclear Engineering
The Pennsylvania State University
University Park, Pennsylvania 16802 (United States)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cnma.201500093.

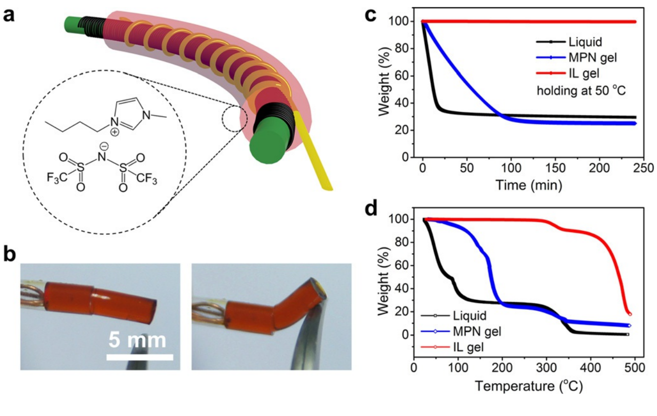

Figure 1. a) Schematic illustration to the structure of a stretchable fiber-shaped dye-sensitized solar cell (DSSC) and the chemical components of ionic liquid (IL) gel electrolyte. b) Photographs of IL gel electrolyte under natural and bending states. c) Weight losses of three different kinds of electrolytes traced at the same temperature of 50 °C. d) Weight losses of three different kinds of electrolytes from room temperature to 500 °C.

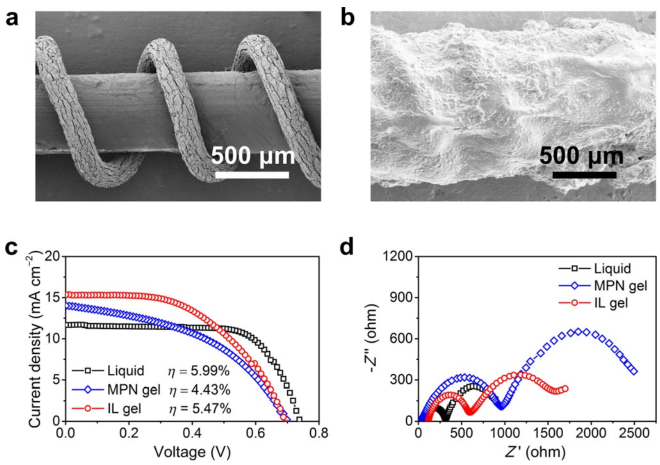

Figure 2. a and b) Scanning electron microscopy (SEM) images of a stretchable fiber-shaped DSSC before and after injection of IL gel electrolyte. c and d) *J–V* and EIS curves of stretchable fiber-shaped DSSCs based on liquid, gel, and IL gel electrolytes.

Et23 purchased from HEPTACHROMA) and MPN-based gel electrolyte.

The solvent vaporization of electrolytes is considered as a major cause for the failure of DSSCs, which is extremely severe for the commercial liquid electrolyte based on volatile acetonitrile (Figure S1). The weight losses of three kinds of electrolytes at 50 °C are traced and compared in Figure 1 c. Due to the vaporization of acetonitrile, the total weight of liquid electrolyte decreased by ≈65 % within 20 min. MPN gel electrolyte demonstrated a longer solvent-containing time of up to 120 min due to the relatively high boiling point of MPN (165 °C) and the formed film by PVDF which slowed down the vaporization of solvent. IL gel electrolyte exhibited the best solvent-containing ability, and the weight remained almost unchanged for 240 min or even longer based on the nonvolatile nature of ionic liquids.

IL gel electrolyte also demonstrates a high stability at high temperature. Thermogravimetric analysis (TGA) tests showed that the IL gel electrolyte did not suffer from obvious weight loss below 300 °C. As a comparison, the acetonitrile-based commercial liquid electrolyte vaporized quickly and even boiled above 80 °C. MPN gel electrolyte lost ≈75 % of the total weight at 200 °C. Differential scanning calorimeter (DSC) characterization was further conducted to measure the melting points of the IL and MPN gel electrolytes. The former produced a melting point of 98.8 °C, higher than the 75.6 °C of the latter (Figure S2). Considering the required high operation temperature of 80 °C for most solar cells,[5,15] the IL gel electrolyte demonstrate a higher thermal stability than the conventional MPN.

To further investigate the performance of IL gel electrolyte, stretchable fiber-shaped DSSCs were fabricated (Figure 1 a).[16] Briefly, a stretchable counter electrode with aligned CNT sheets wound on the surface of a rubber fiber was inserted into a helix-shaped photoanode, which consisted of dye-sensitized TiO_2 nanotube arrays growing on a Ti wire (Figure 2 a). The assembled photoanode and counter electrode were further inserted into a transparent plastic tube, followed by the injection of electrolyte using an injection syringe. Electrolytes would fill between two electrodes due to a surface tension. Gel electrolytes can be heated above the gelation point to produce a uniform solution and then used according to the same injecting procedure. Due to the strength and flexibility of the gel electrolyte, the resulting DSSC can be pulled out of the plastic tube, exposing directly in the air without encapsulation to perform stability tests (Figure S3). The scanning electron microscope (SEM) image showed an intact surface without any cracking of the electrolyte, indicating a high flexibility and stability of the IL gel electrolyte (Figure 2 b).

The *J–V* curves of the fiber-shaped DSSCs based on different electrolytes are compared in Figure 2 c. The effective areas of DSSCs were calculated as the projected area of the anode using an integral method according to the previous report.[16] The DSSC with an IL gel electrolyte produced a power conversion efficiency of 5.47 %, comparable to 5.99 % of a liquid electrolyte.[17] For the MPN gel electrolyte, the power conversion efficiency was much lower (i.e., 4.43 %.) It should be noted that the open circuit voltages of the DSSCs with different electrolytes were slightly different. For the DSSCs based on the same electrode material, it can be ascribe to the different energy levels of different electrolytes caused by the change of iodine–iodide ratios.[18] The high ionic concentration in IL inhibited the ionization of iodide, so the IL gel electrolyte produced a lower V_{OC} but higher J_{SC} than the liquid electrolyte (Table 1).

The inner resistances and ionic mobilities of different electrolytes were compared using electrochemical impedance spectroscopy (EIS) (Figure 2 d). They shared a double semicircle in the curve shape. The first semicircle corresponded to the charge transfer resistance of the interface between the counter electrode and electrolyte, while the second semicircle corresponded to intermediate frequency, referring to the resistance between working electrode and electrolyte. There may also be a third semicircle that corresponded to low frequencies referring to the Warburg impedance inside electrolyte.[19] However, the third semicircle merged into the second semicircle and did

Table 1. Photovoltaic performances of fiber-shaped DSSCs with three different kinds of electrolytes. They were measured under the same conditions.[a]

Electrolyte	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	η [%]
Liquid	0.74	11.65	69	5.99
MPN gel	0.70	13.89	46	4.43
IL gel	0.70	15.32	51	5.47

[a] Average value of five samples for each kind of electrolyte with deviation less than 5%.

not show up in all three curves, indicating that the impedance of electrolyte was low enough to be ignored. This phenomenon has often happened due to high mobilities of iodine ions.[20] The IL gel electrolyte displayed a resistance that was lower than the MPN gel electrolyte while higher than the liquid electrolyte, which also agreed with the result in the power conversion efficiency measurements.

Considering the practical applications of DSSCs, the stability is another important factor that determines the performance of DSSCs. Since IL gel electrolyte overcomes the problems of leakage and vaporization, fiber-shaped DSSCs based on IL gel electrolyte demonstrated a much longer lifetime than the other two electrolytes. After storing for 30 days with UV-cured resin sealing the two ends of the tube, more than 90% of the initial power conversion efficiency could be remained. As a strong contrast, only 40% and 20% could be maintained for the MPN and liquid electrolyte, respectively (Figure 3a). The differences were even more prominent in the case without sealing. The IL gel could preserve nearly 100% of its original power conversion efficiency after 400 min, while MPN gel and liquid electrolytes suffered from a rapid decline during the first 200 min. Accordingly, only ≈71% and 39% of the original power conversion efficiencies were maintained (Figure 3b) due to the vaporization of solvents, which also agreed with the weight loss result in Figure 1c.

Humidity is another factor that causes the failing of a DSSC due to the desorption of dye caused by the attack of water.[8] Based on the hydrophobic nature of BMITFSI, the IL gel electrolyte inherited an excellent resistance to water. To confirm this conclusion, fiber-shaped DSSCs based on different electrolytes were immersed in water at 25 °C for up to 60 min, and the power conversion efficiencies were traced over time. For the encapsulated case, the DSSC based on the IL gel electrolyte preserved over 95%, the MPN gel electrolyte could only maintain 60%, while the liquid electrolyte even failed in less than 40 min (Figure 3c). To meet many practical applications, fiber-shaped DSSCs without encapsulation were immersed in water for 1 min. The DSSC using the IL gel electrolyte could maintain 90% (Figure S4), while the DSSCs from both MPN gel and liquid electrolyte failed immediately due to the dissolution of acetonitrile and MPN in water. The high humid stability makes the IL gel electrolyte very promising for applications under high humidity.

Thermal stability also represents an important aspect for the application of DSSCs, particularly, for some conditions with intensive incident light, which can generate a high temperature

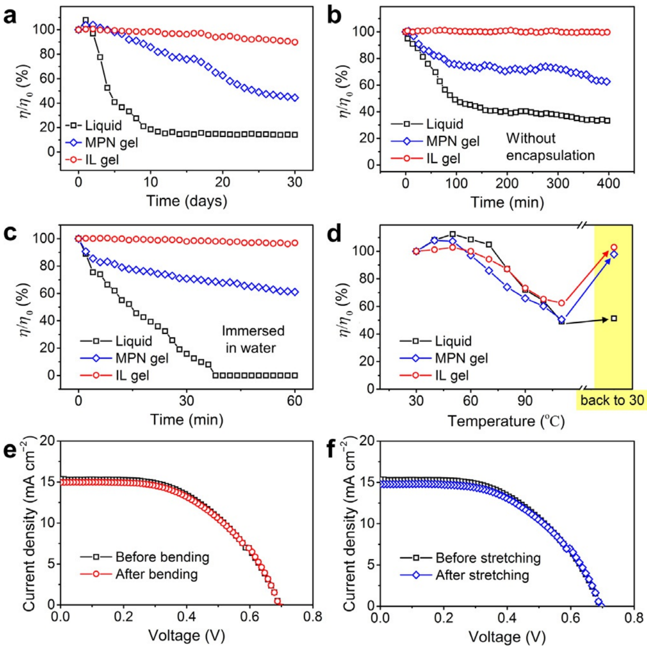

Figure 3. a) Lifetime test of DSSCs derived from the three electrolytes. b) Comparison of the stability of the DSSCs derived from the three electrolytes in air without encapsulation. c) Comparison on the stability of the DSSCs derived from the three electrolytes in water. d) Comparison on the changes of power conversion efficiencies in DSSCs derived from the three electrolytes with gradually increasing temperatures from 30 to 130 °C, followed by decrease to 30 °C. e and f) *J–V* curves of the DSSC derived from the MPN gel after bending with a curvature of 5 mm^{-1} for 10 cycles or stretching to 25% for 10 cycles.

of over 80 °C.[15] To compare the thermal stability, the power conversion efficiencies of fiber-shaped DSSCs based on different electrolytes were traced under heating from 30 to 110 °C (Figure 3d). The power conversion efficiencies shared a trend, that is, a slight increase at temperatures below 50 °C and then a monotonous decrease beyond the point. After cooling down to 30 °C, the DSSC based on the IL gel electrolyte can fully recover the original power conversion efficiency, the DSSC using MPN gel electrolyte recovered ≈95%, while the DSSC from the liquid electrolyte suffered a permanent damage due to the vaporization of solvents, which agreed with the TGA result in Figure 1d.

Based on this novel IL gel electrolyte, the resulting DSSC can be also made to be flexible and stretchable. For instance, the fiber-shaped DSSC was bent at a curvature of 5 mm^{-1} (Figure S5a–c), and the *J–V* curves did not show obvious changes in power conversion efficiency after bending for 10 cycles (Figure 3e). The DSSC can be stretched by 25% for 10 cycles without sacrifice in the power conversion efficiency too (Figure 3f, S5d and S5e and Video S2). The power conversion efficiency of the DSSC could be maintained by above 97% and 95% after bending and stretching, respectively (Figure S6). Note that stretchable polymer solar cells were fabricated but with low power conversion efficiencies (up to 1.2%).[21] In addition, stretchable DSSCs were also produced with higher power conversion efficiencies (up to 7.13%),[16] but the low stability of used liquid electrolytes had largely decreased the device stability. Here the stretchable DSSC based on the IL gel electrolyte showed relatively both high power conversion efficiency and stability.

In summary, a novel gel electrolyte has been developed from PVDF-HFP as a gelata and hydrophobic IL BMITFSI as the solvent to combine the advantages of nonleaking gel and non-volatile ionic liquid. Fiber-shaped DSSCs using this electrolyte demonstrate high flexibility, stretchability, and stability besides a high power conversion efficiency of 5.47%. This work also provides a general and effective strategy in the advancement of high-performance energy harvesting devices.

Acknowledgements

This work was supported by MOST (2011CB932503), NSFC (21225417), STCSM (12nm0503200), the Fok Ying Tong Education Foundation, the Program for Special Appointments of Professors at Shanghai Institutions of Higher Learning, the Program for Outstanding Young Scholars from the Organization Department of the CPC Central Committee and the visiting fund from the State Key Laboratory of Molecular Engineering of Polymers.

Keywords: dye-sensitized solar cells · gel electrolyte · ionic liquids · stretchable

[1] X. Fan, Z. Z. Chu, F. Z. Wang, C. Zhang, L. Chen, Y. W. Tang, D. C. Zou, *Adv. Mater.* **2008**, *20*, 592 – 595; M. R. Lee, R. D. Eckert, K. Forberich, G. Dennler, C. J. Brabec, R. A. Gaudiana, *Science* **2009**, *324*, 232 – 235.
[2] Z. Yang, H. Sun, T. Chen, L. Qiu, Y. Luo, H. Peng, *Angew. Chem. Int. Ed.* **2013**, *52*, 7545 – 7548; *Angew. Chem.* **2013**, *125*, 7693 – 7696.
[3] Y. Bai, Y. M. Cao, J. Zhang, M. Wang, R. Z. Li, P. Wang, S. M. Zakeeruddin, M. Gratzel, *Nat. Mater.* **2008**, *7*, 626 – 630.
[4] M. Gorlov, L. Kloo, *Dalton Trans.* **2008**, 2655 – 2666.
[5] P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi, M. Gratzel, *Nat. Mater.* **2003**, *2*, 402 – 407.
[6] S. Pan, H. Lin, J. Deng, P. Chen, X. Chen, Z. Yang, H. Peng, *Adv. Energy Mater.* **2015**, *5*, 1401438.
[7] J. H. Wu, S. C. Hao, Z. Lan, J. M. Lin, M. L. Huang, Y. F. Huang, L. Q. Fang, S. Yin, T. Sato, *Adv. Funct. Mater.* **2007**, *17*, 2645 – 2652.
[8] H. Tanaka, A. Takeichi, K. Higuchi, T. Motohiro, M. Takata, N. Hirota, J. Nakajima, T. Toyoda, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1143 – 1148.
[9] Q. Li, J. Zhao, B. Sun, B. Lin, L. Qiu, Y. Zhang, X. Chen, J. Lu, F. Yan, *Adv. Mater.* **2012**, *24*, 945 – 950.
[10] S. Li, L. Qiu, C. Shi, X. Chen, F. Yan, *Adv. Mater.* **2014**, *26*, 1266 – 1271.
[11] H. Li, Z. Yang, L. Qiu, X. Fang, H. Sun, P. Chen, S. Pan, H. Peng, *J. Mater. Chem. A* **2014**, *2*, 3841.
[12] M. G. Kang, K. M. Kim, K. S. Ryu, S. H. Chang, N. G. Park, J. S. Hong, K. J. Kim, *J. Electrochem. Soc.* **2004**, *151*, E257 – E260; T. Asano, T. Kubo, Y. Nishikitani, *J. Photochem. Photobiol. A* **2004**, *164*, 111 – 115.
[13] G. Cheruvally, J. K. Kim, J. W. Choi, J. H. Ahn, Y. J. Shin, J. Manuel, P. Raghavan, K. W. Kim, H. J. Ahn, D. S. Choi, C. E. Song, *J. Power Sources* **2007**, *172*, 863 – 869.
[14] S. Abbrent, J. Plestil, D. Hlavata, J. Lindgren, J. Tegenfeldt, A. Wendsjo, *Polymer* **2001**, *42*, 1407 – 1416.
[15] M. Grätzel, *J. Photochem. Photobiol. A* **2004**, *164*, 3 – 14.
[16] Z. Yang, J. Deng, X. Sun, H. Li, H. Peng, *Adv. Mater.* **2014**, *26*, 2643 – 2647.
[17] S. E. Koops, B. C. O'Regan, P. R. F. Barnes, J. R. Durrant, *J. Am. Chem. Soc.* **2009**, *131*, 4808 – 4818.
[18] Z. Yu, M. Gorlov, J. Nissfolk, G. Boschloo, L. Kloo, *J. Phys. Chem. C* **2010**, *114*, 10612 – 10620.
[19] C. He, Z. Zheng, H. L. Tang, L. N. Zhao, F. Lu, *J. Phys. Chem. C* **2009**, *113*, 10322 – 10325.
[20] Q. Wang, J.-E. Moser, M. Grätzel, *J. Phys. Chem. B* **2005**, *109*, 14945 – 14953.
[21] D. J. Lipomi, B. C. Tee, M. Vosgueritchian, Z. Bao, *Adv. Mater.* **2011**, *23*, 1771 – 1775.

Manuscript received: July 1, 2015
Accepted Article published: July 21, 2015
Final Article published: July 31, 2015