Angewandte
Zuschriften

Solid Electrolytes

DOI: 10.1002/ange.201405691

Poly(dimethylsiloxane)-Supported Ionogels with a High Ionic Liquid Loading**

*Ariel I. Horowitz and Matthew J. Panzer**

Abstract: *The immiscibility of poly(dimethylsiloxane) (PDMS) and ionic liquids (ILs) was overcome to create PDMS-supported IL gels (ionogels) with IL loadings of up to 80 % by mass through a simple sol–gel reaction at room temperature. By stirring a mixture of a functionalized PDMS oligomer, formic acid, and an IL (or lithium-in-IL solution), a resin was formed that could be cast to create a freestanding, flexible ionogel. PDMS-supported ionogels exhibited favorable ionic conductivity (ca. 3 $mS\,cm^{-1}$) and excellent mechanical behavior (elastic modulus: ca. 60 kPa; fatigue life: > 5000 cycles; mechanically stable at temperatures up to 200 °C). The activation energy of ionic conductivity was shown to be nearly identical for the ionogel and the neat IL, in contrast to ionogel systems wherein the scaffold material is miscible with the IL. This similarity indicates that IL/scaffold chemical interactions are key to the understanding of ionogel electrical performance, especially at elevated temperatures.*

Supported ionic liquid-based composites, also known as "ionogels," have garnered interest in recent years, as they offer many of the benefits of ionic liquids (ionic conductivity, nonvolatility, nonflammability) in an immobilized solid or solidlike form. These novel hybrid materials are being considered for use as catalytic or separation membranes, as well as solid electrolytes for energy-storage devices.[1–21] Researchers have explored a multitude of different materials as the solid scaffold material for the fabrication of ionogels. Inorganic oxide supports, especially silica scaffolds (prepared both by the ex situ addition of nanoparticles and in situ sol–gel reactions) are straightforward to integrate with an IL and do not limit the thermal stability of the final product.[18–21] A few researchers have proposed organic/inorganic hybrid supports to improve mechanical characteristics while maintaining high thermal stability.[16,17] Unfortunately, the complex syntheses of these hybrid scaffolds often require long reaction times at elevated temperatures.

There have been many reports characterizing gels containing organic polymer supports, which can demonstrate a flexible mechanical character.[7–15] However, many polymers possess limited thermal stability. Moreover, the choice of polymer is often restricted by the limited miscibility of certain polymers in ILs, especially at high degrees of polymerization. Another approach has been to employ cosolvents to overcome immiscibility barriers, thus leading instead to a need for time- and energy-intensive drying processes.[11,12] As a result, there is great interest in understanding the limits of polymer solubility in ILs and how one might overcome them.[1,22,23]

Poly(dimethylsiloxane) (PDMS) is a well-known inorganic polymer with a large variety of industrial applications. The popularity of PDMS is due to its many favorable properties, which include optical transparency, elasticity, and greater stability with respect to a large range of chemical and thermal stresses as compared to many organic polymers.[24] The high thermal and chemical stability of PDMS make it an intriguing candidate for use as the supporting scaffold material in ionogels. However, PDMS is immiscible with many ILs of interest. Although IL/PDMS combinations based on commercial PDMS kits have been proposed in the field of separation membranes, these materials are ionic liquid-poor owing to the difficulty in uniformly combining the IL and PDMS, and have therefore been of limited utility.[25–27] Herein we describe a facile method to overcome the immiscibility between PDMS and ILs to create PDMS-supported ionogels with a high ionic-liquid loading. This new class of materials demonstrates elastic mechanical response, favorable electrical performance when used as a solid electrolyte, and high thermal stability.

PDMS-supported ionogels were formed by a simple, in situ sol–gel reaction to create a cross-linked PDMS network from a functionalized PDMS oligomer by using formic acid (FA) as a catalyst. This reaction scheme was first used with simple silicon alkoxides, such as tetramethyl- and tetraethylorthosilicate (TMOS, TEOS).[20,28] It is well-suited for the preparation of ionogels, as unlike those of some acid-catalyzed sol–gel reactions, all of the reactive by-products are volatile (e.g. ethanol, water) and evaporate within days of ionogel casting.[21] Moreover, FA, TMOS, and TEOS are soluble in many ILs of interest. In this incarnation, the silicon source is a PDMS oligomer with triethoxysilylethyl-terminated end groups (f-PDMS, MW = 700–900). These functionalized end groups serve as three reactive sites per oligomer end, analogous to the four reactive sites of TEOS.

To overcome the immiscibility of f-PDMS and the IL, it is necessary to stir a mixture of FA, IL, and f-PDMS until a stable resin is obtained (Figure 1 a). At this point, the mixture can be cast and allowed to cure in situ to produce a solid, freestanding gel (Figure 1 b). The end groups of the f-PDMS must come into proximity with the FA in the IL phase

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[*] A. I. Horowitz, Prof. M. J. Panzer
Department of Chemical and Biological Engineering
Tufts University
4 Colby Street, Medford, MA 02155 (USA)
E-mail: matthew.panzer@tufts.edu
Homepage: http://ase.tufts.edu/genelab/home.html

[**] This research was performed with financial support from the National Science Foundation (award no. ECCS-1201935) and the US Army Natick Soldier Research, Defense and Engineering Center.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201405691.

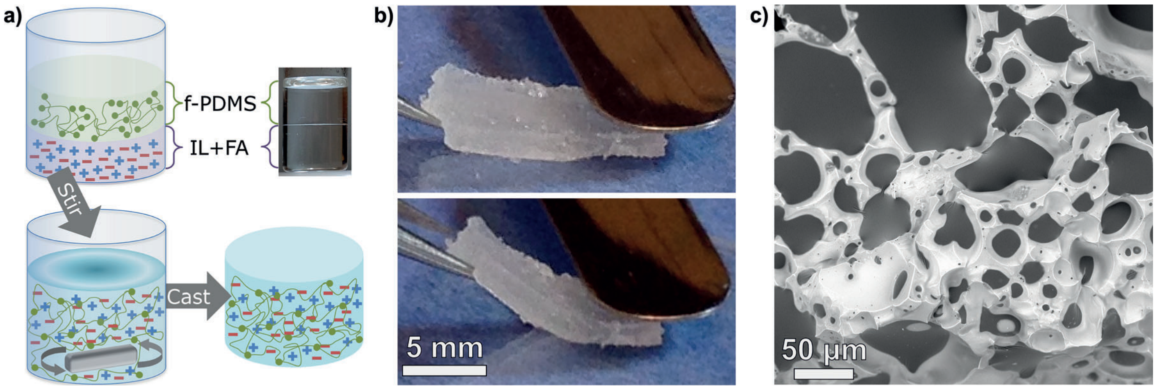

Figure 1. Preparation and images of PDMS ionogels. a) Photograph highlighting the immiscibility between the f-PDMS and IL layers without agitation, and schematic diagram of the preparation of PDMS ionogels. The liquid f-PDMS oligomer of lower density (top layer) is not miscible with the ionic-liquid/formic acid (IL + FA) solution (bottom layer). The cross-linking sol–gel reaction is initiated upon stirring the mixture; after a sufficient period of mixing, the resin can be cast into any arbitrary shape, thus resulting in a freestanding material containing the IL intermixed with cross-linked PDMS. b) Photographs (showing ionogel flexibility) of an unbent (top) and bent sample (bottom) of the PDMS ionogel. c) SEM image of the ionogel structure, showing the ionic liquid (dark-gray regions) immobilized by a solid, spongelike PDMS scaffold (lighter regions).

to react. Agitation of the system during the reaction creates a comingled mixture of the growing PDMS network within the IL, resulting in a spongelike structure (Figure 1c) with domains of pure IL contained within a porous PDMS scaffold. By this synthetic strategy, PDMS-supported ionogels with high IL loadings may be formed by using a variety of ILs. PDMS-supported ionogels incorporating large mass fractions of 1-ethyl-3-methylimidazloium bis(trifluoromethylsulfonyl)imide (EMI TFSI), 1-butyl-3-methylpyrrolidinium (BMP) TFSI, and EMI tetracyanoborate (TCB) were all successfully created by this approach, as well as ionogels incorporating lithium TFSI. Herein, we focus on the properties of pure EMI TCB-based ionogels owing to the outstanding conductivity of this IL.[14] For the formulation used in this study, a 30 min mixing time was required to produce a resin, which then cured over several hours to create ionogels that contained 80 % IL by mass, as compared to 5–50 % reported previously.[25–27]

The structure of the PDMS-supported ionogels (Figure 1c) was significantly different to that of some other ionogel types, especially silica-supported ionogels, in which nanostructured silica is in intimate contact with the IL throughout the ionogel.[18,22] The PDMS scaffold was sparsely cross-linked, with a molecular weight between cross-links of approximately 11 000 $\mathrm{g\,mol^{-1}}$ (see the Supporting Information). However, all oligomer chains were incorporated into the final scaffold structure (see Figure S1 in the Supporting Information). This structure is consistent with the observation that the sol–gel reaction network may terminate at different extents of condensation, rather than proceeding to complete cross-linking at every reactive site.[29] Furthermore, despite the comparatively open pore structure of the PDMS-supported ionogels, freestanding samples displayed no IL leakage over time. The PDMS-supported ionogels were also stable upon exposure to water, thus mitigating concerns regarding water infiltration, which can limit the operating voltage of electrochemical devices.

The ionogel displayed an elastic modulus of approximately 60 kPa and demonstrated elastic deformation up to at least 30 % compressive strain with only minor hysteresis (Figure 2). Signs of yield begin at approximately 45 % strain, after which the hysteretic effect was increased. Although it contained 80 % IL by mass, the ionogel showed solidlike behavior over a wide frequency range (Figure 2, inset). Some stiffening was observed at high frequencies, in agreement with previous reports.[30] PDMS-supported ionogels could withstand over 5000 cycles of mechanical stress and maintained mechanical integrity above 200 °C (see Figures S2 and S3).

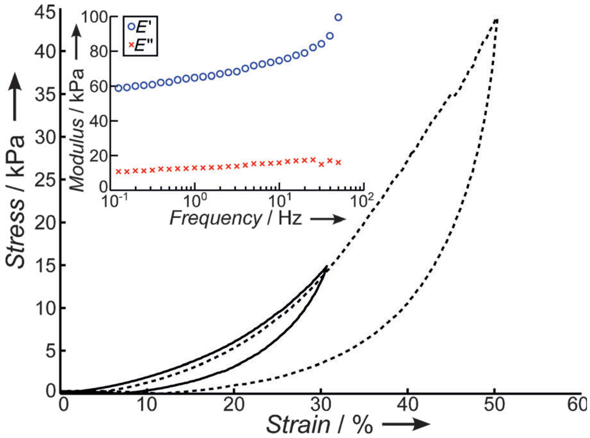

Figure 2. Ionogel mechanical characteristics. Stress–strain curves show elastic deformation until at least 30% compressive strain, with only minor hysteresis. Signs of yield are initially seen at roughly 45 % strain. Inset: Frequency sweep of the ionogel dynamic mechanical response, showing some stiffening at high frequencies. The storage modulus (E') is larger than the loss modulus (E'') across the frequency range studied, thus indicating solidlike behavior.

The cross-linked PDMS scaffold is thermally stable until at least 200 °C (Figure 3). The differential scanning calorimetry (DSC) trace of a PDMS-supported ionogel showed only the EMI TCB melting transition, which occurs at 10 °C. No glass or melting transitions of PDMS occur within the studied temperature range.[31] The DSC trace of pure PDMS (as-

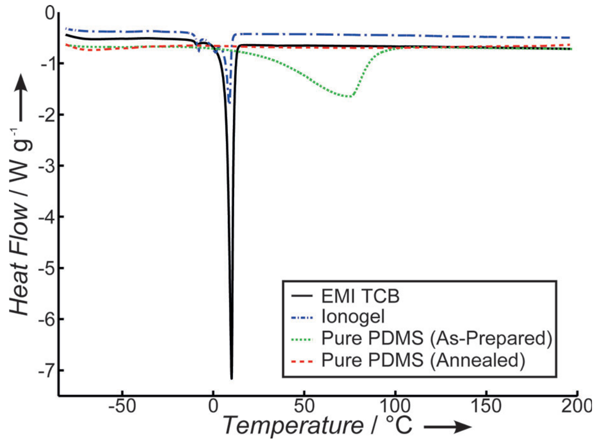

Figure 3. DSC heating traces for the neat ionic liquid (EMI TCB), PDMS-supported ionogel, and pure PDMS both as-prepared and postannealing. Both EMI TCB and the ionogel show an IL melting peak at 10 °C. The as-prepared PDMS trace shows a broad transition indicating the presence of unreacted end groups in the 20–75 °C range. This transition disappears after the PDMS is annealed at 50 °C for several hours. The ionogel shows no such transition, thus indicating that the scaffold cross-linking reaction is complete.

prepared) showed a broad transition above 0 °C that indicates the presence of unreacted f-PDMS end groups. This transition disappeared after annealing of the pure PDMS sample at 50 °C for several hours. No such transition was observed in the DSC trace of the as-prepared PDMS-supported ionogel. Similarly, a disappearance of some of the peaks associated with the reactive end groups of f-PDMS was observed in the FTIR spectrum of the ionogel (see Figure S4).

The PDMS-supported ionogels described herein are suitable for use as solid electrolytes in supercapacitor devices, with a room-temperature ionic conductivity of 3.1 mS cm^{-1} (Figure 4), which is well above the benchmark of 1 mS cm^{-1} desired for use in electrochemical devices.[32] When tested in a double-layer capacitor structure, PDMS-supported ionogels also demonstrated clear capacitive behavior (see Figure S5). Although the ionogel conductivity is lower than that of neat EMI TCB (12.6 mS cm^{-1}), the observed activation energy of ionic conductivity for the ionogel (14.6 kJ mol^{-1}) is nearly identical to that of the neat IL (14.4 kJ mol^{-1}) and similar to previously reported values for EMI TCB-based ionogels.[14] By contrast, the incorporation of scaffold materials with which ILs are miscible has been shown to lead to changes in the activation energy of conductivity for the corresponding ionogels.[7] This result reinforces the notion that for ionogels with immiscible IL/scaffold pairs, there exists only a physical barrier to ionic motion as a result of the presence of the scaffold, as opposed to any thermally sensitive energetic or chemical interactions between the IL and the solid support.

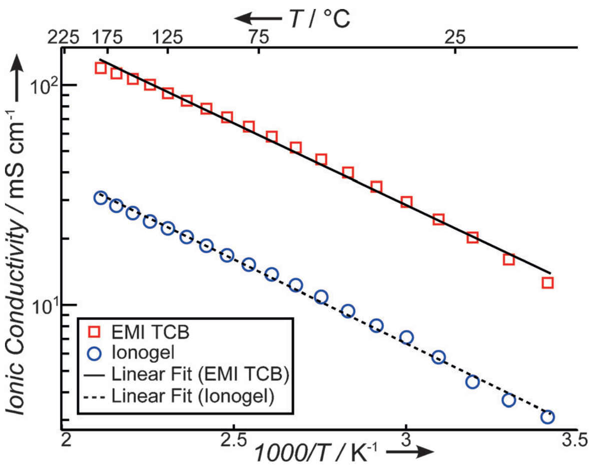

Figure 4. Arrhenius plots of ionic conductivity for a PDMS-supported ionogel and for neat EMI TCB. The ionic conductivity of the ionogel is lower than that of the neat IL, but the two activation energies are nearly identical.

Continued optimization of the fabrication process is expected to lead to a lower minimum achievable scaffold content for PDMS-supported ionogels and thus larger values of ionogel conductivity. Moreover, Li^{+}-containing ionogels (see the Supporting Information) may be promising candidates for safer battery electrolytes with further development.

Ionogels are an emerging class of materials with tremendous potential for use in a variety of applications. Through the use of a simple sol–gel reaction under ambient conditions, a new type of ionogel containing a PDMS scaffold was fabricated, thus overcoming the barrier of immiscibility between PDMS and ILs or lithium-in-IL solutions. The ionogels described herein demonstrate a favorable combination of thermal stability, ionic conductivity, and elastic mechanical behavior. Moreover, they exhibit an activation energy of conductivity nearly identical to that of the neat ionic liquid. Besides the favorable combination of properties exhibited by PDMS-supported ionogels, the synthetic technique employed in this study offers insight into how ILs may be combined with otherwise incompatible scaffold materials more generally, thereby opening the door to the further creation of novel ionogels.

Received: May 27, 2014
Revised: June 24, 2014

Keywords: composite materials · gels · ionic liquids · sol–gel processes · solid electrolytes

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[1] J. Le Bideau, L. Viau, A. Vioux, *Chem. Soc. Rev.* **2011**, *40*, 907–925.
[2] T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.
[3] S. S. Moganty, N. Jayaprakash, J. L. Nugent, J. Shen, L. A. Archer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9158–9161; *Angew. Chem.* **2010**, *122*, 9344–9347.
[4] Y. Gu, C. Ogawa, J. Kobayashi, Y. Mori, S. Kobayashi, *Angew. Chem. Int. Ed.* **2006**, *45*, 7217–7220; *Angew. Chem.* **2006**, *118*, 7375–7378.
[5] Y. Xiong, J. Liu, Y. Wang, H. Wang, R. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9114–9118; *Angew. Chem.* **2012**, *124*, 9248–9252.
[6] T. Zhang, H. Zhou, *Angew. Chem. Int. Ed.* **2012**, *51*, 11062–11067; *Angew. Chem.* **2012**, *124*, 11224–11229.
[7] M. A. B. H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J. Am. Chem. Soc.* **2005**, *127*, 4976–4983.

[8] D. F. Miranda, C. Versek, M. T. Tuominen, T. P. Russell, J. J. Watkins, *Macromolecules* **2013**, *46*, 9313 – 9323.
[9] D. W. Kim, D. Y. Chi, *Angew. Chem. Int. Ed.* **2004**, *43*, 483 – 485; *Angew. Chem.* **2004**, *116*, 489 – 491.
[10] L. C. Branco, J. G. Crespo, C. A. M. Afonso, *Angew. Chem. Int. Ed.* **2002**, *41*, 2771 – 2773; *Angew. Chem.* **2002**, *114*, 2895 – 2897.
[11] Y. Gu, S. Zhang, L. Martinetti, K. H. Lee, L. D. McIntosh, C. D. Frisbie, T. P. Lodge, *J. Am. Chem. Soc.* **2013**, *135*, 9652 – 9655.
[12] K. H. Lee, S. Zhang, T. P. Lodge, C. D. Frisbie, *J. Phys. Chem. B* **2011**, *115*, 3315 – 3321.
[13] J. Lee, M. J. Panzer, Y. He, T. P. Lodge, C. D. Frisbie, *J. Am. Chem. Soc.* **2007**, *129*, 4532 – 4533.
[14] G. P. Pandey, S. A. Hashmi, *J. Mater. Chem. A* **2013**, *1*, 3372.
[15] A. F. Visentin, M. J. Panzer, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2836 – 2839.
[16] F. Gayet, L. Viau, F. Leroux, F. Mabille, S. Monge, J.-J. Robin, A. Vioux, *Chem. Mater.* **2009**, *21*, 5575 – 5577.
[17] J. Le Bideau, M. Y. Miah, A. Vioux, F. Fajula, A. Galarneau, *J. Mater. Chem.* **2010**, *20*, 964 – 971.
[18] K. Ueno, K. Hata, T. Katakabe, M. Kondoh, M. Watanabe, *J. Phys. Chem. B* **2008**, *112*, 9013 – 9019.
[19] Y. Lu, S. K. Das, S. S. Moganty, L. A. Archer, *Adv. Mater.* **2012**, *24*, 4430 – 4435.
[20] M.-A. Néouze, J. Le Bideau, A. Vioux, *Prog. Solid State Chem.* **2005**, *33*, 217 – 222.
[21] A. I. Horowitz, M. J. Panzer, *J. Mater. Chem.* **2012**, *22*, 16534 – 16539.
[22] K. Ueno, T. Fukai, T. Nagatsuka, T. Yasuda, M. Watanabe, *Langmuir* **2014**, *30*, 3228 – 3235.
[23] N. Winterton, *J. Mater. Chem.* **2006**, *16*, 4281 – 4293.
[24] J. C. Lötters, W. Olthuis, P. H. Veltink, P. Bergveld, *J. Micromech. Microeng.* **1997**, *7*, 145 – 147.
[25] P. Izák, K. Friess, V. Hynek, W. Ruth, Z. Fei, J. P. Dyson, U. Kragl, *Desalination* **2009**, *241*, 182 – 187.
[26] P. Izák, W. Ruth, Z. Fei, P. J. Dyson, U. Kragl, *Chem. Eng. J.* **2008**, *139*, 318 – 321.
[27] N. L. Mai, S. H. Kim, S. H. Ha, H. S. Shin, Y.-M. Koo, *Korean J. Chem. Eng.* **2013**, *30*, 1804 – 1809.
[28] K. G. Sharp, *J. Sol-Gel Sci. Technol.* **1994**, *2*, 35 – 41.
[29] L. L. Hench, J. K. West, *Chem. Rev.* **1990**, *90*, 33 – 72.
[30] H. H. Winter, *J. Rheol.* **1986**, *30*, 367.
[31] A. Shefer, M. Gottlieb, *Macromolecules* **1992**, *25*, 4036 – 4042.
[32] M. W. Schulze, L. D. McIntosh, M. A. Hillmyer, T. P. Lodge, *Nano Lett.* **2014**, *14*, 122 – 126.