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Introduction

Hybrid ionogel electrolytes for high temperature lithium batteries†

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Hybrid ionogels fabricated using 1 M LiTFSI in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMPTFSI) crosslinked with ladder-like structured poly(methacryloxypropyl)silsesquioxane (LPMASQ) were investigated as high temperature ionogel electrolytes for lithium ion batteries. In addition to the exceedingly low crosslinker concentration (~2 wt%) required to completely solidify the ionic liquids, which provided high ionic conductivities comparable to the liquid state ionic liquid, these hybrid ionogels exhibited superior thermal stabilities (>400 °C). Rigorous lithium ion battery cells fabricated using these hybrid ionogels revealed excellent cell performance at various C-rates at a variety of temperatures, comparable with those of neat liquid electrolytes. Moreover, these hybrid ionogels exhibited excellent cycling performance during 50 cycles at 90 °C, sustaining over 98% coulombic efficiency. Highly advantageous properties of these hybrid ionogels, such as high ionic conductivity in the gel state, thermal stability, excellent C-rate performance, cyclability and non-flammability, offer opportunities for applications as high temperature electrolytes.

Ionic liquids have been widely investigated as possible solutions for the next generation of electrolytes in electrochemical cells due to their advantageous properties of high ionic conductivity, high electrochemical stability, non-flammability, negligible vapour pressure and high thermal stability.^{1,2} Despite these advantages over lithium salt solutions,^{3,4} ionic liquid electrolytes still face the problems of leakage and low cycling properties, which has proved to be a serious concern for some applications, for instance in fully electronic or hybrid vehicles.² To solve the problem of leakage in liquid electrolytes, research on gel polymer electrolytes (GPEs) has been pervasive in electrochemical device applications, such as capacitors and lithium ion batteries.5-7

Gel polymer electrolytes can be defined as a class of electrolytes in which the liquid electrolyte is either swollen in

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polymers or crosslinked through thermally or photo-initiated processes.8,9 Extensive reports have detailed the utility of organic polymers as a matrix or crosslinkable oligomers/polymers as crosslinking agents.8-10 Furthermore, GPEs can be classified depending on the type of solidified liquid electrolyte solution, as ionogels are GPEs composed of solidified ionic liquids.11 Many ionogels have been fabricated using a variety of structural support materials, including polymers, colloidal particles, carbon nanotubes and crosslinkable small organic molecules.12 While these approaches have been proved to be extremely useful for the fabrication of gels and films, considerable amounts of matrix or crosslinking agent compared with the liquid electrolyte needed for the solidification of ionic liquids have had major depreciating effects on the electrochemical device performances.12 Therefore, minimal use of the crosslinking agent, while maintaining non-flowing, solid-like behaviour, has remained a challenge for optimal electrochemical devices.

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Inorganic-organic hybrid materials, such as silicon-oxide based materials, have also garnered great interest as the support matrix for ionogels for their favourable properties, for instance, thermal stability, electrochemical stability and facile processing.13-22 Several studies have detailed the electrochemical studies and Li battery applications with chemically modified siloxanes, such as commercially available $[RSiO_{1.5}]_n$ polysilsesquioxane-based ORMOCERS,²³ or [SiO₂]_n silica-based materials, as the ionogel support matrix.13-17 These approaches have either entailed the use of organic crosslinking functionalities or the in situ sol-gel gelation of ionic liquids using

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hydrolytic or non-hydrolytic sol–gel processes.¹³⁻¹⁷ Notable studies by Vioux¹⁵⁻¹⁷ and Panzer¹³ groups have detailed the *in situ* gelation of ionic liquids to yield ionogels with tunable flexibility. However, the fabrication of these ionogels by *in situ* sol–gel reactions may have a number of long-term problems in the solid state, as uncondensed silanol groups may produce water molecules through secondary condensations. Additionally, organic acids, such as formic acid, which are used for catalyzing the sol–gel hydrolysis-condensation rearrangements, may not be completely removed *in vacuo*, thus remaining as impurities. The long times (5 days to 2 weeks) needed to solidify the ionic liquid *in situ* is also a process unfavourable for industrial applications.¹⁴

Another class of hybrid gel polymer electrolytes include composites of oxide particles. Functional silane-coated oxidebased nanoparticles,24-27 which have been rigorously investigated by the Archer group, and 'soggy sand' electrolytes, which have been investigated by Bhattacharyya²⁸⁻³⁰ are representative examples of such composites. Surface modification of oxidebased nanoparticles coated with functional silanes (e.g., ionic liquid groups, oligo-polyethylene oxide groups, and single ion conducting groups) provides excellent electrochemical stability and mechanical robustness compared with the neat liquid electrolytes.24 Soggy sand electrolytes, which comprise oxide particles dispersed in non-aqueous liquid solutions, have also been widely investigated as structurally supporting agents to solidify the liquid electrolytes.²⁸⁻³¹ However, for applications in lithium ion batteries, these hybrid gel polymer electrolytes should provide impeccable dispersion in liquid electrolytes to achieve well-defined homogeneous composites. The mechanical properties of these materials are still too low for such an application. These are issues that still need to be addressed and thoroughly investigated for practical lithium ion battery applications.

Polysilsesquioxanes (PSQs) with chemical formula $[RSiO_{1.5}]_n$ are a class of inorganic–organic hybrid materials in which a silicon oxide network structure is equipped with an organic functionality.³² There are three structural classes of PSQs, random-branched network, polyhedral cage and ladder-like polymers. Although polyhedral cage structures, also known as polyhedral oligomeric silsesquioxanes (POSS), have been used as crosslinkers or additives,^{33–36} their generally low solubility³⁷ has limited their applications as composites with ionic liquids. In addition, as mentioned above, ionogels fabricated from random-branched structural PSQ-modified silica particles suffer from remnant silanol groups that will condense to form water molecules over time, making their applications in Li batteries practically infeasible.

Ladder-like structured polysilsesquioxanes (LPSQs) are a unique class of silsesquioxanes in which the siloxane bond is double stranded and the organic functional groups are unidirectionally positioned to the siloxane bonds.^{37–42} These materials exhibit enhanced solubility and superior thermal stability because of the imperceptible amount of silanol groups, which only reside at the polymer end groups.^{37–42} The acid resistance and insensitivity to thermal history characters can also be said to be the highly attractive merits of these materials as polymer

⁷ Notable electrolytes. The polymeric nature of these materials allows for the introduction of several hundreds of organic moieties per polymer chain for a fast and easy curing process.^{37,38} Recently, our research group developed a facile, one-pot synthesis of Doblems in LPSQs using a base-catalyzed system.^{37–40} The products of the synthesis were fully condensed high molecular weight LPSQs. Additionused for mer electrolytes, these materials are highly soluble in nonaqueous electrolytes and ionic liquids, leading to high homogeneity, whereas they need only a small amount of gelator. In this study, we synthesized a novel ladder-structured polyumethacrylowyropyl)silsesquioxane (LPMASQ) following our

(methacryloxypropyl)silsesquioxane (LPMASQ) following our method and used it as a crosslinker for an ionic liquid electrolyte, 1 M LiTFSI in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPTFSI). Thermal crosslinking of the methacryl moieties of LPMASQ resulted in homogeneous, non-leaking hybrid ionogels. The thermal, mechanical and flame-retardant properties of these inorganic–organic hybrid gel polymer electrolytes were examined and Li battery cells were fabricated to test their applications as thermally stable and high performance ionogels.

Experimental

Materials

3-Methacryloxypropyltrimethoxysilane (Shin-Etsu, 98%) and ethyl acetate (J.T. Baker, HPLC grade) were distilled over CaH_2 prior to use. Potassium carbonate (Daejung) was dried at 40 °C. THF (J.T. Baker, HPLC grade) was distilled over sodium. Azobisisobutyronitrile (Daejung) was recrystallised from methanol. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (Aldrich, 99.9%, battery grade), 1-methylpyrrolidine (Aldrich, 98%), 1iodobutane (Aldrich, 99%) and all other solvents were used as received.

Synthesis of LPMASQ

LPMASQ was synthesized following a known literature procedure.^{37–40} In a typical experiment, potassium carbonate, K_2CO_3 (0.04 g, 0.29 mmol), was dissolved in deionised H_2O (4.8 mL, 0.27 mol) and 8 g of THF was added. To this solution, 3-methacryloxypropyltrimethoxysilane (19.9 mL, 0.08 mol) was added dropwise under nitrogen flow. The solution was magnetically stirred for 10 days when the molecular weight reached its maximum value. After partial evaporation of THF, the resinous material was dissolved in dichloromethane and extracted several times with water. Collection of the organic layers followed by drying of the organic layer over anhydrous magnesium sulphate and evaporation of the solvent under reduced pressure yielded a transparent liquid with medium viscosity (15.2 g, 95% crude yield). LPMASQ was found to have excellent solubility in the majority of organic solvents.

¹H NMR (CDCl₃) (δ , ppm): (0.48–0.78, SiCH₂CH₂CH₂CH₂-OCOCCH₂CH₃), (1.5–1.75, SiCH₂CH₂CH₂OCOCCH₂CH₃), (3.9– 4.1, SiCH₂CH₂CH₂OCOCCH₂CH₃), (5.4, 5.9, SiCH₂CH₂CH₂-OCOCCH₂CH₃), (1.75–1.85, SiCH₂CH₂CH₂OCOCCH₂CH₃), ¹³C NMR (CDCl₃) (δ , ppm): (7.6–10.3, SiCH₂CH₂CH₂OCOCCH₂CH₃), (17.5–18.5, SiCH₂CH₂CH₂CH₂OCOCCH₂CH₃), (21.2–22.4, SiCH₂CH₂-CH₂OCOCCH₂CH₃), (65.4–66.8, SiCH₂CH₂CH₂OCOCCH₂CH₃), (124.4–126.1, SiCH₂CH₂CH₂OCOCCH₂CH₃), (135.5–136.9, SiCH₂CH₂CH₂OCOCCH₂CH₃), (166.6–168.6, SiCH₂CH₂CH₂CH₂-OCOCCH₂CH₃), ²⁹Si NMR (ppm): –65 to –68 ppm, $M_{\rm w} = 26\ 000$ g mol⁻¹, $M_{\rm w}/M_{\rm n} = 2.1$.

Synthesis of *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

Synthesis of BMPTFSI was performed following a literature procedure.⁴³ In a dry 500 mL round-bottom flask, stoichiometric amounts of 1-methylpyrrolidine (50 g, 0.59 mol) and 1-iodobutane (108 g, 0.59 mol) in 250 mL of ethyl acetate were magnetically stirred at room temperature for 24 h. The product was repeatedly washed with ethyl acetate and filtered until a pure white salt of BMPI was obtained. BMPI was then dissolved in deionized water and mixed with a stoichiometric amount of LiTFSI dissolved in deionized water. The organic phase was extracted with methylene chloride and subsequently dried at 100 °C for 24 h to remove any residual water. The resulting BMP–TFSI had a H₂O content of less than 100 ppm as measured using the Karl Fischer method. The ¹H NMR characterization of BMPTFSI is shown in the ESI, Fig. S1.[†]

Preparation of hybrid ionogels

In an inert, argon-charged glove box, solutions with various amounts of LPMASQ in 1 M LiTFSI in BMPTFSI were prepared in a glass vial. An amount of 1 wt% (relative to LPMASQ) of AIBN as a thermal initiator was added to this solution. After taking the solutions out of the glove box, samples were sonicated and shaken for 10 min or until the solution was homogeneous. Then, the samples were directly taken to an oven preset at 70 °C for 3 h. The hybrid ionogels were named as HI-2 and HI-5 for ionogels containing 2 and 5 wt% of LPMASQ, respectively.

Characterisation and measurements

Fourier transform infrared spectra were recorded with a Perkin-Elmer FT-IR system Spectrum-GX. Number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of polymers were measured using a JASCO PU-2080 plus SEC system equipped with a refractive index detector (RI-2031 plus), UV detector ($\lambda = 254$ nm, UV-2075 plus) and a Viscotek SLS apparatus using THF as the mobile phase at 40 °C with a flow rate of 1 mL min⁻¹. The samples were separated through four columns (Shodex-GPC KF-802, KF-803, KF-804, KF-805). ¹H-NMR and ²⁹Si NMR spectra were recorded in CDCl₃ at 25 °C using a Varian Unity INOVA (¹H: 300 MHz, ²⁹Si: 59.6 MHz). Thermal gravimetric analysis was carried out with a TA instrument (TGA 2950) at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere.

Rheological properties were examined using a rheometer (Advanced Rheometric Expansion System, ARES) instrument with cone-plate geometry (25 mm diameter). All rheological measurements were performed in the linear viscoelastic region under a nitrogen atmosphere.

The ionic conductivity was determined using a complex impedance analyzer (Bio-Logics, VMP3) over a frequency range from 1 Hz to 1 MHz at an AC amplitude of 10 mV. The electrochemical stability of the gel polymer electrolytes was examined using a linear sweep voltammetry system. In the experiments, a stainless steel working electrode was used with lithium metal as both the counter and reference electrodes. The voltage was swept at a scan rate of 1.0 mV s⁻¹. The time evolution dependence of the interfacial resistance between the lithium metal and the ionogel was measured through monitoring the AC impedance response over the frequency range from 100 kHz to 10 MHz of the Li/HI-2/Li symmetric cells. Electrochemical measurements of the gel polymer electrolyte were conducted using 2032 coin cells consisting of a separator, Li metal and a LiFePO₄ cathode (90 wt% LiFePO₄, 5 wt% carbon black, and 5 wt% PVDF). All the cells were assembled in an argon-charged glove box. After fabrication, the cells with pre-gel solution were subjected to thermal cross-linking for 3 h at 70 °C. The galvanostatic charge-discharge experiments were carried out in the voltage range of 2.5-4.2 V using a battery cycler (Wonatech, WBCS3000) at room temperature.

Results and discussion

Inorganic-organic hybrid ionogel fabrication

The synthesis and characterization of LPMASQ has been previously reported.³⁷ This facile and mass-producible method for production of highly condensed ladder-like structured polysilsesquioxanes has been proved to be extremely useful for high yield production of LPSQs. The obtained LPMASQ was then dissolved in an ionic liquid solution of 1 M LiTFSI in BMPTFSI with various amounts of AIBN as a thermal initiator (Scheme 1). Through mild thermal treatment at 70 °C, non-leaking, homogeneous hybrid ionogels were able to be easily processed as freestanding gels (Scheme 1, inset). As shown in the right-hand side model, we expected that the LPMASQ network being formed after crosslinking was loose enough to facilitate high lithium mobility within the LPMASQ network. The obtained hybrid ionogels were HI-2, HI-5 containing 2 and 5 wt% of LPMASQ, respectively.

Through extensive pre-trials, we observed that LPMASQ was capable of completely solidifying BMPTFSI, even at an exceedingly low concentration of 2 wt% (HI-2). As shown in Fig. 1, the peaks assigned to the C=C bonds at 1635 cm⁻¹ completely disappeared after the curing process, demonstrating that the cross-linking reaction was completed. The inset photograph in



Scheme 1 Fabrication of hybrid ionogels.

Paper



Fig. 1 FTIR spectra of hybrid ionogel HI-5 before and after thermal curing with an inset photograph.

Fig. 1 shows that the ionic liquid electrolyte was completely solidified after thermal curing. Similar to our previous study,³⁷ we demonstrated that LPMASQ was able to produce mechanically pliant and non-flowing gel polymer electrolytes using only a mere 2 wt% of the gelator. This stable formation of homogeneous ionogels led us to hypothesize optimal electrochemical performance with these hybrid ionogels.

Rheological properties of hybrid ionogels

Rheological examinations of gel polymer electrolytes and hybrid ionogels have recently been found to be an efficient method to elucidate the mechanical properties of such soft materials.24-29 Fig. 2a presents the changes of dynamic viscoelastic properties of neat BMPTFSI and hybrid ionogels as a function of angular frequency. For the neat BMPTFSI, the loss modulus G'' was found to be greater than the storage modulus G'. Both dynamic modulus values exhibited power law dependency over the experimental range, which is a typical rheological characteristic of a viscous fluid.^{29,30} These results clearly demonstrate the dynamic shift from a liquid to solid-like state; predominantly elastic behaviour with only minimal addition of LPMASQ due to the well-developed network structure. Meanwhile, with increasing LPMASQ concentration, the network structure becomes denser, resulting in an increase in the gel rigidity, as is evident by the increase in the dynamic modulus order. Furthermore, as shown in Fig. 2b, the thermal scanning rheological observation for hybrid ionogel HI-2 showed that storage modulus values were stable at temperatures exceeding 250 °C.

Thermal stability

The thermal stability of electrolytes is a critical requirement for their safety and stability in lithium ion battery applications. The TGA thermograms of LPMASQ, BMPTFSI and two kinds of prepared hybrid ionogels are presented in Fig. 3. As shown, the initial degradation temperatures of LPMASQ and BMPTFSI are very similar (\sim 400 °C), but LPMASQ left residual silica at



Fig. 2 Rheological properties of hybrid ionogels (a) frequency sweep and (b) temperature sweep.

temperatures exceeding 500 °C. The residual mass of the hybrid ionogels at various concentrations also correlated well with the LPMASQ concentration as ionogels with higher LPMASQ concentration gave greater residual mass at 800 °C. Given the exceedingly high initial degradation temperature of these hybrid ionogels, it can be said that these materials exhibit superior thermal stability. Moreover, thermal shrinkage tests with the neat ionic liquid compared with a HI-2 impregnated polypropylene (PP) separator were conducted at 150 °C for 30 minutes (Fig. 3b). As shown, the neat ionic liquid impregnated PP separator showed significant shrinkage, while the HI-2 impregnated PP separator showed exceptionally low thermal shrinkage, indicating that these hybrid ionogels have superior thermal and thermo-mechanical properties for use at elevated temperatures.

Electrochemical properties of hybrid ionogels

Ionic conductivity. The temperature dependency of the ionic conductivity of gel polymer electrolytes produced with various amounts of cross-linker was examined *via* the AC impedance spectroscopy technique. The ionic conductivity (σ) of an electrolyte can be described using the following equation.³⁶



Fig. 3 (a) TGA thermograms of BMPTFSI, LPMASQ, and hybrid ionogels and (b) thermal shrinkage tests with neat ionic liquid and HI-2 impregnated polypropylene separators.

$\sigma(T) = \Sigma n \times q \times \mu$

where *n* is the number of charge carriers, *q* is the charge on the charge carrier, and μ is the mobility of charge carriers. Hybrid ionogels fabricated through the gelation of the liquid electrolyte can provide good mechanical properties, though at the cost of sacrificing ionic conductivity. The ionic mobility (μ) correlated with the diffusion of ions is hindered when compared with 1 M LiTFSI in the BMPTFSI electrolyte due to the formation of a network structure. Furthermore, a decrease in the number of the charge carriers (n) per unit volume of the electrolyte, caused by the introduction of the crosslinking agent, is also a contributing factor for the restricted ionic conductivity. A notable advantage of this work is the gelation of the ionic liquid with 2 wt% LPMASQ. Due to the minimal amount of gelator content used to fabricate these free-standing hybrid ionogels, high ionic conductivity similar to the neat BMPTFSI was expected. As shown in Fig. 4, a decrease in ionic conductivity was observed for hybrid ionogels with increasing amounts of LPMASQ. However, the ionic conductivity of HI-2 was observed to be 0.79 mS cm⁻¹ at 30 °C, which is in close proximity to the ionic conductivity of the neat ionic liquid electrolyte (0.96 mS cm^{-1}). In addition, we plotted the ionic conductivities of a commercially available organic-based crosslinker (ETPTA) utilized in several previous studies.44 As shown, the high amounts of ETPTA required for full solidification of 1 M LiTFSI



Fig. 4 Temperature dependency of ionic conductivities of hybrid ionogels.

BMPTFSI led to the drastic decrease in ionic conductivities and subsequent poor cell performance to be discussed later.

Electrochemical stability. The electrochemical stability of electrolytes over the operating voltage of a lithium-ion battery is also an important requirement for practical battery operation. The linear sweep voltammetry (LSV) measurements were performed at potentials between 3.0 and 7.0 V (V vs. Li/Li⁺) under various temperature conditions. As shown in Fig. 5, upon the voltage sweep, the onset of the oxidation current increase, which is related to the electrochemical oxidative decomposition of the electrolyte, shifted closer to 5.0 V with increasing temperature. Greater slopes of I-E diagrams were also observed at higher temperatures, indicating that the oxidation current depends on the test temperature. However, no significant oxidation current was observed below 5.0 V even at elevated temperatures, demonstrating that the obtained gel polymer electrolytes were electrochemically stable up to 5.0 V, which could be applied to high-voltage lithium batteries over a wide temperature range.



Fig. 5 Linear sweep voltammograms of hybrid ionogel HI-2 at various temperatures.

Interfacial stability towards the Li metal electrode. To evaluate the compatibility of Li metal electrodes with hybrid ionogels, the interfacial resistance of the Li/HI-2/Li test cell was monitored during a period of 25 days. Fig. 6 shows the time evolution of the AC impedance spectra under open-circuit potential conditions. The intercept with the Z_{real} axis at high frequency presents the bulk resistance (R_s) , which remained stable and constant with the storage time, confirming the stability of ionogels against the lithium metal. In comparison, the mid-frequency semicircle associated with the interfacial resistance (R_{int}) gradually increased with time until a steady state was reached (ESI, Fig. S2[†]). Such a response could be explained by the formation of a passivation layer on the lithium metal electrode surface that suppresses continuous electrochemical reactions between the lithium metal electrode and electrolyte, resulting in the stabilization after a few days of storage.45,46 The electrochemical behaviour of the hybrid ionogel toward lithium metal was further investigated by conducting cyclic voltammetry (CV) of a symmetrical Li/HI-2/Li cell. As ESI Fig. S3[†] reveals, the cell underwent a reversible redox process with high coulombic efficiency, and the peak current of the CV profile tended to decrease with increase in the cycle number. These results also confirm the stabilization at the interface, suggesting that the compatibility of the ionogel towards the lithium metal electrode is sufficient for application in lithium batteries.

Cell performance. To characterize the electrochemical performance of hybrid ionogels, we fabricated coin cells using LiFePO₄ as the cathode and metallic lithium counter electrodes assembled with HI-2 (98 wt% of ionic liquid containing 2 wt% LPMASQ). Fig. 7a presents the discharge capacity of the cells at various temperatures. During the examination, the cells were charged at a constant current density of 0.1 C (1 C rate corresponded to a current density of 155.1 mA g⁻¹) and discharged at various current densities in a voltage range of 2.5–4.2 V. As shown, the cells delivered stable discharge capacity upon repeated cycling at various current rates. However, the discharge



Fig. 6 Nyquist plot of AC impedance for a Li/HI-2/Li cell.



Fig. 7 (a) Discharge capacity at various temperatures and C-rates for LiFePO₄/HI-2/Li cells, (b) representative discharge profile at different temperatures for LiFePO₄/HI-2/Li cells cycled under 0.1 C charge-0.1 C discharge conditions.

capacity and voltage of cells gradually decreased when the discharging current density rate increased. This lower discharge capacity is attributed to the increase in cell polarization caused by the poor kinetics at the electrode–electrolyte interface.⁴⁷ With increasing temperature, as expected, the discharge capacity of the cell increased. For instance, in the initial cycle at 50 °C, the discharge capacity with a current density of 0.5 C was 88.3 mA h g⁻¹, whereas cells cycled at 90 °C delivered a greater discharge capacity of 156.2 mA h g⁻¹, which is close to the theoretical discharge capacity of the cathode active material in this potential region (170 mA h g⁻¹ for LiFePO₄).

Typical discharge profiles of the cell fabricated using HI-2 at various temperatures with 0.1 C charge–0.1 C discharge are displayed in Fig. 7b. In general, a flat voltage plateau at approximately 3.4 V (ν s. Li/Li⁺) corresponds to the conversion between LiFePO₄ and FePO₄.^{47,48} A well-defined voltage plateau was observed above 50 °C, whereas the truncated flat voltage region and the voltage drops were observed at 30 °C. These results clearly show that the limited conversion process is mainly due to the low diffusion of lithium-ions in both electrolytes and the cathode material, indicating that a sufficient mobility of lithium ions is required to maintain the electrochemical performance of batteries.



Fig. 8 Cyclability of HI-2 compared with a conventional organic ionogel fabricated using ETPTA, with the inset figure showing the representative discharge profiles for HI-2.

The cycling stability of the cells at 90 °C was evaluated further through measurement of the discharge capacity. The cells were charged at a current density of 0.2 C and discharged at 0.5 C. Fig. 8 shows the cycling performance of the cell prepared using our hybrid ionogels and the discharge profiles at various cycles (Fig. 8, inset), in comparison with the cells prepared using a well-known organic crosslinker, ETPTA-based ionogel.44 The structure of ETPTA is shown in the ESI, Fig. S4.† The cells containing HI-2 ionogels exhibited relatively stable cycling performance. In addition, the discharge capacities for HI-2 were comparable to cells containing the liquid 1 M LiTFSI BMPTFSI (ESI, Fig. S5[†]). The discharge capacity was maintained at a value of 147.1 mA h g^{-1} after 50 cycles, which was 94.9% of its largest discharge capacity and the columbic efficiency of the system was found to be above 98% with the exception of cell activation. Moreover, no obvious change in the charge-discharge profiles or significant capacity decay were observed, confirming the thermal stability and electrochemical stability of the ionogels. In comparison, the cells containing an organic crosslinker ETPTA-based ionogel exhibited a rapid capacity loss over a repeatable cycling process and the discharge capacity decreased to 118.7 mA g^{-1} , which is a capacity retention of 82.7%, the greatest discharge capacity after being cycled merely 50 times. It should be noted that HI-2 was able to fully solidify the ionic liquid at a mere 2 wt%, whereas the organic ionogel fabricated using ETPTA required a high concentration of the cross-linker (15 wt%), which caused the significantly lower ionic conductivity compared with HI-2 (Fig. 4). Therefore, the improved electrochemical performances of the cell with ionogels could be ascribed to the less dense network-structure formed by LPMASQ, which could help to minimize the depreciation of the lithium-ion diffusion of the gel polymer electrolyte, resulting in enhanced electrochemical performances.

Conclusions

Inorganic-organic hybrid ionogels were fabricated using thermally curable LPMASQ as a high temperature gel polymer

electrolyte in Li batteries. Using an extremely simple mix and cure system, these hybrid ionogels exhibited thermal stability beyond 400 °C, stable mechanical properties at high temperatures and ionic conductivities on a par with the neat ionic liquid. Li battery cell tests revealed that these hybrid ionogels could deliver high specific capacity and good cycling performance at elevated temperature, demonstrating the possible application of hybrid ionogels in Li batteries.

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