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High strain stretchable solid electrolytes

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Abstract

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Keywords

high, stretchable, strain, solid, electrolytes

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Abstract

Wearable electronic devices that can be integrated seamlessly into clothing for monitoring and feedback need to be not only flexible, but also stretchable with low stiffness. Currently there are few solid electrolytes that are sufficiently stretchable for wearable electronic devices. Here we report stretchable solid electrolytes that can be elastically stretched more than 500% of their original length with ionic conductivities as high as $7 \times 10^{-5} \text{ S cm}^{-1}$ and tensile breaking strengths larger than 1.5 MPa. These solid electrolytes consist of poly(methyl methacrylate) chemical networks solvated by an electrochemically stable ionic liquid. A stretchable supercapacitor was demonstrated by coating a stretchable solid electrolyte with carbon nanotube electrodes.

Highlights

- Stretchable and flexible solid electrolyte with elastic strains larger than 500% and ionic conductivities as high as $7 \times 10^{-5} \text{ S cm}^{-1}$.
- Stretchable and flexible supercapacitor with capacitance of 4 F g^{-1} .

Keywords

Stretchable electronics; solid electrolyte; ionogel; ionic liquid, poly(methyl methacrylate); supercapacitor

1. Introduction

Stretchable electronics refers to stretchable components and circuitry[1]. Examples include electronic skin[2] which monitors body functions whilst having a compliance similar to human skin, soft bionic interfaces like electrophysiological sensors[3], and, stretchable batteries and supercapacitors[4-7]. The key to any stretchable device is the maintenance of electronic properties at different tensile extensions. The extension required is application dependent, and varies from a few percent for a compliant neural interface to several hundred percent for electronic clothing.

Most reported stretchable electronic devices consist of rigid electron conducting components mounted in a stretchable rubber film or matrix, or, mesh like constructs from non-elastic materials which are able to undergo large elastic deformation via localized bending[1].

Energy storage devices are an essential element of any electronic textile system. As such considerable attention has been paid to the development of stretchable electrodes [5, 7-9]. Surprisingly the development of robust stretchable electrolytes that mechanically reinforce the electrochemical cell in which they are located has earned relatively little attention.

One approach to synthesizing stretchable electrolytes is to form a polymer network within an ionic liquid. The conductivity and negligible volatility inherent to all ionic liquids make them ideal electrolytes [10]. For many applications, encapsulation of individual stretchable electrochemical cells is difficult which makes negligible volatility a necessary property. Several ionic liquids also exhibit a wide electrochemical window which can be exploited in electrochemical supercapacitors [11, 12].

Ionic liquids have also been shown to be an exceptional solvent for free radical polymerisation[13]. For example, it is known that both high molar mass and high yield can be achieved relative to more common organic solvents. It follows that a network synthesized in an ionic liquid should have fewer defects and superior mechanical properties in comparison to networks synthesized from the same polymer in common organic solvents.

High compliance and flexible electrolytes have been prepared by forming polymer networks within a range of ionic liquids, and the resulting solids are referred to as ionogels[14-18]. Approaches to synthesizing chemically cross-linked polymer networks within ionic liquids include free radical polymerisation, and, chemically crosslinking a prepolymer[18]. Outstanding ionogels were produced by Fujii *et al.* exhibiting very high ionic conductivities ($7.7\text{-}8.5\text{ mS cm}^{-1}$) and tensile breaking strains (310%-380%), but low tensile strengths of just 15-33 kPa[18]. Although there are many reports of flexible solid ionogel electrolytes, few report high elastic mechanical properties, and, few have attempted to demonstrate their function in a stretchable electrochemical cell.

We report here the fabrication of highly stretchable solid electrolytes by free radical polymerisation and demonstrate their application in stretchable supercapacitors.

The motivation for the present work is to construct stretchable solid electrolytes with sufficient strength to support electrodes and eliminate the need for additional mechanical reinforcement. This research will enable the development of fully stretchable electrochemical cells. Here, the function of a solid electrolyte is not just an ionic conductive spacer sandwiched between electrodes, but also a vital mechanical element.

2. Method

Stretchable transparent solid electrolytes were synthesized by free radical polymerization of MMA (Aldrich) with polyethylene glycol diacrylate (PEGDA) crosslinker (Aldrich) with a number average molar mass of 285 g mol^{-1} in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMI.TFSI) (Australian National Fabrication Facility). EMI.TFSI was synthesized as described in [19] with an additional purification step of purging with Argon at 30°C . The water content of the EMI.TFSI was measured by Karl Fisher to be $\leq 0.3\%$. A weight ratio of MMA to EMI TFSI of 1:1 was used for all synthesis. Neat EMI.TFSI has a conductivity of $8 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C [20]. Radical polymerization was thermally initiated (80°C) using 0.5 mol % methyl ethyl ketone peroxide (Aldrich).

0.8 mm transparent thick free standing ionogel films were formed by injecting the mixed reagents into a mold consisting of two glass plates separated by a silicone rubber gasket. The glass plates were coated with octadecyltrichlorosilane to reduce adhesion to the formed electrolytes. Prior to polymerisation, the solutions were purged with nitrogen for 10 minutes within the moulds to reduce oxygen. The samples were then placed in an oven at 80°C for 24 h where polymerization took place.

For mechanical testing, ionogels were cut into ISO 37 Type 3 dumbbell shape test pieces (gauge length 10 mm). Samples were subjected to tensile tests with a crosshead speed of 5 mm min^{-1} using an Instron 5566 universal testing machine.

The ionic conductivity of the ionogels was determined by electrochemical impedance using a two electrode configuration. The solid electrolytes were cut into 100 mm^2 square pieces and then mounted between two single 100 nm thick platinum coated indium tin oxide (ITO) glass

electrodes that were clamped at a constant force of 156 N with a Bessey XC5™ series clamp. The impedance spectra were recorded from 50 mHz to 100 kHz with an amplitude of 10mV using a Gamry EIS 3000™ system instrument. The reported conductivity was taken at a frequency of 100 kHz. Prior to all measurements, the open circuit potential was monitored in order to ensure the system was stable.

The electrochemical stability of the ionogels was determined by cyclic voltammetry over the potential range of 0 V to 6 V relative to Li|Li⁺ at room temperature over a scan rate of 1 mV.s⁻¹. Solid electrolyte samples were mounted in between stainless steel and Li foil electrodes in a LR 2032 type coin cell configuration assembled in a glove box under an argon atmosphere.

A symmetric stretchable supercapacitor was assembled by drop-casting a 1 mg ml⁻¹ dispersion of functionalized multi-walled carbon nanotubes (CNT) in dimethylformamide (DMF) on both sides of an ionogel with a prestrain of 30%. Upon evaporation of the DMF, the CNT films function as stretchable supercapacitor electrodes. Electrical contacts to the CNT films were made by copper tape. Prior to drop casting, CNT with an outer tube diameter of 30-50 nm and length of 10-20 μm (Chengdu Organic Chemicals Co. Ltd.) were functionalized by mixing into an acid solution consisting of H₂SO₄ and HNO₃ (3:1) using a sonication bath (Branson B5500R-DTH) until a suspension was formed with no CNT particles observed by eye. The functionalized CNT were dispersed into dimethylformamide (DMF) (1 mg ml⁻¹) by probe ultrasonication. The surface morphology of the supercapacitor electrodes was investigated by means of a cold-field-gun field emission microscope (FESEM, JEOL JSM7500FA). Electrochemical characterisation of the supercapacitor was conducted

in air on the laboratory bench with the specific capacitance of the supercapacitor calculated as described in[21].

3. Results and discussion

The produced ionogels were capable of undergoing extraordinary strain before break. Their mechanical properties are more than adequate to mechanically reinforce a stretchable electrochemical cell. The elongation to break increased whilst the elastic modulus decreased with an increase to the cross-linker density (Fig. 1a). Strains as large as $6\times$ the original length were achieved. The engineering failure stress was greater than 1.5 MPa for all samples, and remained independent of cross-link density even though the molar ratio of cross-linking molecule to monomer was varied over an order of magnitude. The elastic modulus was between 10 and $3\times$ less than the failure stress and increased from 130 to 470 kPa as the mol % of crosslinker was increased from 0.5 to 5. The gels with just 0.5 mol % crosslinker are likely to have a homogenous density network as the modulus was 87% of that predicted by rubber elasticity for a model network. A model network assumes that there is 100% yield from polymerisation, and, that there are no dangling chain ends. Clearly, the use of 0.5 mol % crosslinker and 0.5 mol% initiator as used here allows efficient low defect polymerisation to proceed. Ionogels formed under the same conditions, but with 1 mol % initiator were flexible, but, exhibited much lower elongation to break. Other reagent ratios may lead to a more fragile network due to a larger defect density. Cyclic tensile tests showed that the samples are elastic at strains up $\sim 90\%$ of the elongation to break.

The ionogels reported here exhibited the behaviour expected of a solvated polymer network. For example, there was no decrease in the tangent modulus prior to failure, confirming that yield prior to failure does not occur, unlike a similar system reported by Matsumoto *et al.* for

similar systems[22, 23]. The tensile breaking strains were more than 10× larger than those reported in the literature for a free radical polymerised ionogel [16, 23]. Of note, the failure strain for both a 1 and 0.5 mol % crosslinked ionogels was larger than **the maximum failure strain (380%)** reported by Fujii et. al. for a polymer network formed from prepolymer[18]. Although a breaking strain of 600% is more than required by most applications, there is no apparent reason why it could not be increased further by decreasing the crosslinker concentration below 0.5 mol %. The elastic modulus of the ionogels was in the same range as that reported for similar systems , but almost 2 orders of magnitude higher than that observed for a prepolymer system with a much higher ionic liquid volume fraction.

Gels with a network structure containing few defects are anticipated to have high mechanical strength[24]. Given the observed high modulus relative to a model network, and, the observed high breaking strains it is complicit that the breaking tensile stress should be high. The breaking strength was several times larger than that reported for similar systems[23]. As expected by the large difference in ionic liquid volume fraction, the breaking stress is also more than 2 orders of magnitude larger than those reported by Fujii et. al. for their high strain prepolymer ionogels[18]. Gayet et. al[17]. described polymer-nanocomposite ionogels with breaking strains and tensile strengths comparable to those reported here (>200% and >3 MPa respectively), however, their system is only elastic at small strains.

Impedance measurements of the ionogels demonstrate its function as an electrolyte (Fig. 1b). The ionic conductance of the ionogels varied between 2×10^{-5} and 7.5×10^{-5} S/cm. The ionic conductivity with 5 mol % crosslinker was less than half that of samples with 0.5 to 2 mol % crosslinker. Generally cross-linking restricts the motion of the polymer backbone and so subsequently may decrease the ionic conductivity.

All of the ionogels were electrochemically stable up to 4.9 V relative to Li|Li⁺. At potentials higher than 4.9 V a large increase in the current was observed where the electrolyte decomposes. The electrochemical window is sufficiently large for many applications including Li-ion batteries and supercapacitors.

Smooth CNT film electrodes were achieved on the solid electrolyte at a prestrain of 30% at which they were deposited (Fig. 2a). When the prestrain was released, the CNT film exhibited a buckled structure due to a difference in the Poisson's ratio of the CNT films and the stretchable electrolyte (inset of Fig. 2b). Symmetric stretchable supercapacitors exhibited nearly rectangular cyclic voltammograms at scan rates of 5 (Fig. 2c) and 10 mV s⁻¹, indicative of highly reversible electric double layer charge-discharge response. The supercapacitor demonstration confirms that the ionic conductivity of the solid electrolyte is sufficiently high for supercapacitor applications. The buckled CNT film retained most of its electrochemical activity. It is apparent that the rectangular shape of the cyclic voltammogram at 0 % strain is distorted relative to that at 30% strain indicating an increased cell resistance. It is likely that the electronic conductivity of the CNT films decreases when the initial prestrain is released. A potential window of 1 V was applied to the supercapacitor as it was tested in air and larger potential windows exhibit electrochemical events associated with oxygen and/or water. An inert atmosphere is required to fully utilize large electrochemical window of the ionogel.

In the as prepared condition at a scan rate of 5 mV s⁻¹ the supercapacitor delivered a capacitance of 6.9 F g⁻¹ of CNT. A slightly lower capacitance of 4.0 F g⁻¹ of CNT was shown for the buckle-structured supercapacitor at the same scan rate. Following 50 stretching cycles

from 0 to 30% strain, and the capacitance slightly decreased to 4.0 and 3.8 F g⁻¹ at 0% and 30% strain respectively. These results clearly demonstrate that the solid stretchable electrolyte can function as a supercapacitor electrolyte between suitable electrodes.

4. Conclusions

Very high strain, moderate strength stretchable ionogels were produced. The ionogel compliance and elongation at break are easily manipulated by changing crosslinker concentration during synthesis. These ionogels exhibited ionic conductivities as high as $7 \times 10^{-5} \text{ S cm}^{-1}$, with a stretchable super capacitor being demonstrated. These ionogels are an ideal solid electrolyte platform for stretchable electrochemical cell applications including electronic skin and textiles. Key properties of the solid electrolytes are negligible volatility and sufficient mechanical properties to reinforce freestanding film electrochemical cells. Application of these stretchable electrolytes is currently limited by development of stretchable electrodes.

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Figure Captions

Figure 1: (a) Tensile test, and, (b) electrochemical impedance studies of ionogels prepared with different crosslinker concentrations.

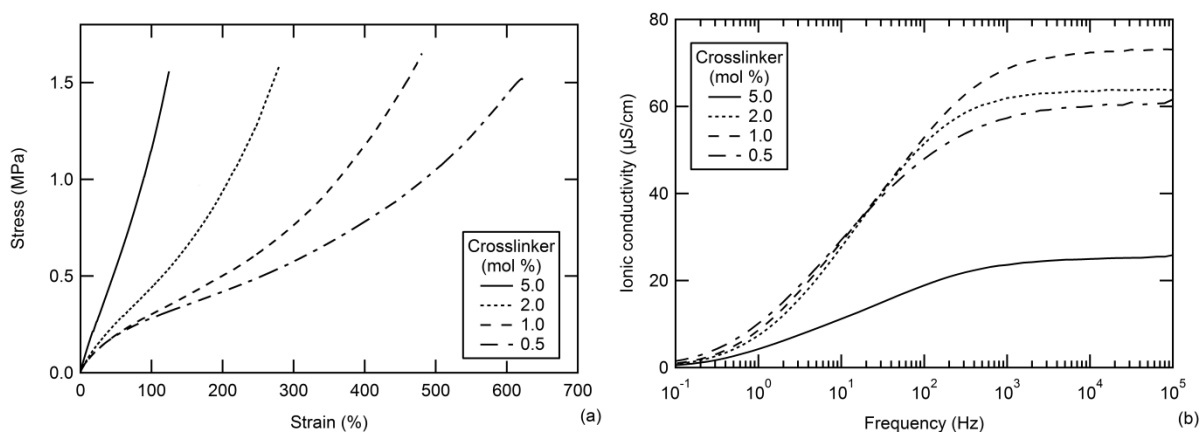


Figure 2. SEM images of the top surface of a CNT coated ionogel as prepared at 30% strain (a) and (b) after relaxation to 0% strain. Cyclic voltammograms of symmetric supercapacitors scanned at 5 mV s^{-1} at 0% and 30% strain before (c) and after 50 stretching cycles at 30% elongation.

