

Short communication

Novel poly(methyl methacrylate)-based semi-interpenetrating polyelectrolyte gels for rechargeable lithium batteries

Saibabu Kalapala, Allan J. Easteal*

Chemistry Department, University of Auckland, Private Bag 92019, Auckland, New Zealand

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Abstract

Novel semi-interpenetrating polymer gel electrolytes designed for use in rechargeable lithium polymer batteries are synthesised from methyl methacrylate and the lithium salt of 2-acrylamido-2-methylpropanesulfonic acid (LiAMPS). The gels are made by first synthesising linear chains of poly(LiAMPS) by free radical polymerisation of LiAMPS dissolved in dimethyl acetamide (DMA) or DMA/ethylene carbonate mixtures, then co-polymerisation of methyl methacrylate and a cross-linking monomer (tetraethyleneglycol diacrylate) to form the semi-interpenetrating network. The electrical conductivity of the gels is determined as a function of LiAMPS and methyl methacrylate (MMA) concentrations, cross-link density, and solvent composition. The conductivity (σ) is found to be in the range $0.2 \leq \sigma \leq 0.8 \text{ mS cm}^{-1}$ at ambient temperature ($20 \pm 1^\circ\text{C}$).

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1. Introduction

Polymer electrolytes have attracted attention in recent times because of their use in lithium batteries, fuel cells, sensors, electrochromic displays, and supercapacitors [1–3]. There is a need to develop advanced battery systems with high specific energy and high efficiency to match the miniaturisation in modern electronic devices such as cell phones, laptop computers, and notebook computers. Furthermore, scaled-up versions of these batteries are being considered for use as energy sources in zero-emission vehicles. Research and development activity world-wide in both academia and industry has been reported in several recent reviews and monographs [4–8].

In contrast to typical solid polymer electrolytes, polymer gel electrolytes can show conductivity comparable with that of liquid electrolytes at ambient temperatures. In polymer gel electrolytes, the polymer gel (e.g., polyacrylonitrile [9,10],

poly(methyl methacrylate) [9,11], or poly(vinylidene fluoride) [12,13]), is swollen in a suitable organic solvent with a high dielectric constant, and doped with a lithium salt such as lithium triflate or hexafluorophosphate to provide lithium-ion conductivity. In these systems, both cations and anions contribute to charge transport, and the transport number of the lithium ions is consequently significantly less than unity.

The disadvantage of polymer gel electrolytes in having a low transport number is essentially eliminated in polyelectrolyte gels in which the anion is covalently bonded to a polymer backbone. The polymer chains, and hence their associated negative charges, have intrinsically small translational mobility. Consequently, only the counterions (such as Li^+) have significant mobility. Moreover, the electrical conductivity of these gels is typically an order of magnitude higher than for conventional polymer gels doped with lithium salts. Thus, in gels based on dimethyl acrylamide/lithium 2-acrylamido-2-methylpropanesulfonate (LiAMPS) copolymers, cross-linked with tetraethylene glycol diacrylate and swollen with ethylene carbonate/dimethylacetamide mixtures [14,15], the transport number of Li^+ is necessarily

* Corresponding author. Tel.: +64 9 373 7599; fax: +64 9 373 7422.
E-mail address: aj.easteal@auckland.ac.nz (A.J. Easteal).

close to unity. Furthermore, conductivities of more than $10^{-3} \text{ S cm}^{-1}$ can be achieved by optimising the gel composition.

In polyelectrolyte gels based on LiAMPS, the backbone polymer chains carrying the negative charges give rise to the ability of the gel to conduct current, and in addition form, with the cross-linking agent, the polymer network. Consequently, the conductivity of the gel and its mechanical properties are inextricably linked, and increasing the conductivity by decreasing the total polymer concentration, for example, produces a softer gel. The roughly inverse relationship between rigidity and conductivity makes it difficult to optimise both mechanical properties and electrical conductivity. In the present work, an attempt is made to circumvent this problem by designing a gel in which the network structure is established with a cross-linked uncharged polymer (PMMA), and cationic charge transport capability is provided by linear poly(LiAMPS) chains embedded in the PMMA network in a semi-interpenetrating fashion. While the (cationic) conductivity is still coupled to the rigidity of the gel, the semi-interpenetrating network structure allows more flexibility in optimisation of mechanical and transport properties. The purpose of this communication is to report conductivity data from an exploratory study on a series of these semi-interpenetrating polyelectrolyte gels in which monomer concentrations and other experimental parameters have been varied with the objective of attaining some insight into the factors that have most effect on the conductivity.

2. Experimental

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) (98%) supplied by Lancaster Synthesis, Li_2CO_3 (AnalaR grade, BDH Chemicals), dimethyl acetamide (99%, Acros Organics), ethylene carbonate (99%, Lancaster Synthesis), methyl methacrylate (99%, Lancaster Synthesis), tetraethyleneglycol diacrylate (technical grade, Aldrich Chemicals), and azobiscyclohexanecarbonitrile (99%, Aldrich Chemicals) were used without further purification, except that dimethyl acetamide was dried with a type 4A molecular sieve before use.

Appropriate amounts (10–30 mmol) of 2-acrylamido-2-methylpropanesulfonic acid and Li_2CO_3 (0.5 mol per mole of AMPS) were dissolved in 20 mL of either dimethyl acetamide or a dimethyl acetamide/ethylene carbonate (EC) mixture in a 100-mL beaker at ambient temperature. A free radical initiator (azobiscyclohexanecarbonitrile, 1 mg mL^{-1}) was added to the solution and allowed to dissolve completely, and the solution was purged with nitrogen. The solution was then heated in a laboratory oven for 60 min at 100°C , to form linear chains of poly(LiAMPS). The resulting viscous liquid was allowed to cool to ambient temperature.

Methyl methacrylate (MMA, 20 or 40 mmol), tetraethyleneglycol diacrylate (TEGDA, 2.5–10 mmol) and azobiscyclohexanecarbonitrile (1 mg mL^{-1}) were added to the cold

poly(LiAMPS) solution, and the solution was ultrasonicated for 15 min to remove air bubbles. The solution was then used to fill a mould that consisted of two silanised glass plates that were separated by a 3-mm thick polytetrafluoroethylene (PTFE) spacer. The filled mould was heated for 60 min at 100°C to form the semi-interpenetrating gel.

Ionic conductivity measurements were made using a spring-loaded sample holder in which the sample was sandwiched between two polished stainless-steel electrodes embedded in PTFE discs. The spring exerted a small pressure on the sample to ensure good contact between the gel sample and the electrodes. The separation of the electrodes, i.e., the thickness of the sample, was determined with a micrometer. The whole arrangement was contained in a glass vessel that could be evacuated or flushed with gas. An ac signal was applied to the electrodes at a fixed frequency of 2 kHz and the resulting current and voltage were measured. Conductivity was calculated using the relationship:

$$\sigma = \frac{Id}{EA} \quad (1)$$

where I and E are the steady-state current and voltage, respectively, d is the thickness of the sample and A is the geometric area of the electrodes.

3. Results and discussion

The gel compositions and conductivity data are given in Table 1. Gels 8 and 9 were made up separately to have the same composition. The conductivities of the two gels were within about 3%, which is the order of the anticipated uncertainty in σ .

The data for gels 2 and 3 indicate that the conductivity is only weakly dependent on the concentration of charge carriers. This was a surprising result, and it may be that varying the LiAMPS concentration over a broader range will reveal a more pronounced variation in the conductivity. From a practical point of view, an AMPS concentration of 1.5 mol L^{-1} (gel 13) instead of 1 mol L^{-1} (gel 10) gives a pregel solution that is too viscous for subsequent mixing with MMA and the cross-linking agent at ambient temperature. It is interesting to note that at an intermediate concentration of AMPS (1.2 mol L^{-1} , gel 14), the conductivity is substantially reduced relative to the corresponding gel with 1 mol L^{-1} AMPS (gel 10). Thus, for the specified concentrations of the other components, and in this range of LiAMPS concentrations, the conductivity varies inversely with the concentration of charge carriers. A similar observation has been reported recently by Georén and Lindbergh [16] for polymer gels doped with LiClO_4 . The behaviour of the gels is also analogous to that of aqueous electrolyte solutions, for which the conductivity typically decreases with concentration at high concentrations of electrolyte.

The rigidity of the gels is determined primarily by the concentrations of cross-linking agent and methyl methacry-

Table 1
Gel compositions and conductivities at ambient temperature

Gel no.	$c(\text{Li}^+\text{AMPS}^-)^a$	$c(\text{MMA})^a$	$c(\text{TEGDA})^a$	wt.% EC	σ (mS cm ⁻¹)
1	1.5	2.0	0.5	0	0.27
2	1.0	2.0	0.25	0	0.28
3	0.5	2.0	0.25	0	0.21
4	1.0	1.0	0.125	0	^c
5	1.0	1.0	0.25	0	0.68 ^d
6	1.0	1.0	0.25 ^b	0	0.76 ^d
7	1.0	1.0	0.5	0	0.33
8	1.0	1.0	0.5	30	0.65
9	1.0	1.0	0.5	30	0.63
10	1.0	1.0	0.5	40	0.84
11	1.0	1.0	0.5	50	^e
12	1.0	1.0	0.5	60	^f
13	1.5	1.0	0.5	40	^g
14	1.2	1.0	0.5	40	0.41
15	1.2	1.0	0.5	50	0.50

^a Concentrations in mol L⁻¹.

^b Cross-linked with ethylene glycol dimethacrylate.

^c Gel was not sufficiently rigid for conductivity measurement.

^d Relatively soft gels.

^e Inhomogeneous gel.

^f Ethylene carbonate crystallised during gel preparation.

^g Poly(Li⁺AMPS⁻) solution was too viscous to allow subsequent mixing with methyl methacrylate and cross-linking agent.

late. When the MMA concentration is reduced from 2 to 1 mol L⁻¹, with a cross-linking agent concentration of 0.25 mol L⁻¹ (gels 2 and 5), the gel becomes too soft for use in practical devices. Halving the cross-linking concentration, hence the cross-link density, leads to a gel (gel 4), which was too soft to allow determination of its conductivity. Comparison of gels 5 and 7 shows that doubling the cross-link density increases the rigidity of the gel to the extent that the conductivity is approximately halved. In passing, it is noted that substitution of ethylene glycol dimethacrylate for tetraethyleneglycol diacrylate, as a cross-linking agent (gels 5 and 6), has a small effect (12% increase) on conductivity. This is possibly due to a different distribution of cross-links relative to the location of the anionic sites on the polyLiAMPS chains.

The most significant experimental variable, in relation to the conductivity of this series of gels, is the solvent composition. Conductivity is a strong function of ethylene carbonate content: increasing the proportion of EC from 0% (gel 7) to 40% (gel 10) increases conductivity by more than 150%. The implication is that EC has a specific effect in relation to the predominant charge transport mechanism that is operating in the gel, for the following reasons. The shear viscosity of DMAc/EC mixtures containing 0–81 wt.% EC has been determined at 30 °C by means of a Ubbelohde viscometers. The data can be represented by:

$$\eta(\text{mPa s}) = 0.8935 + 5.201 \times 10^{-3} F + 6.194 \times 10^{-5} F^2 + 1.140 \times 10^{-7} F^3 \quad (r^2 = 0.9992) \quad (2)$$

where F = mol% EC. Interpolation of the equation for η gives a viscosity of 1.21 mPa s for a solvent mixture with 40 wt.% EC, which is more than 30% greater than for pure DMAc.

The total concentration of monomers and cross-linking agent in the gels was at most 4 mol L⁻¹ (in gel 1), so that the solvent content of the gels was at least 60% by weight. It is reasonable to assume, therefore, that gel 10 has a higher viscosity than gel 7 due to the higher proportion of EC in gel 10. On the basis of the Stokes equation, and in the absence of other contributing factors, gel 10 would most likely have a smaller conductivity than gel 7, which is not in accordance with the experimental observations.

A likely intramolecular mechanism for charge transport in these gels can be visualized as Li⁺ ions hopping between negatively charged sites on the backbone chains. As a first approximation, it is assumed that the negatively charged sites are fixed in space, i.e., the translational mobility of the polyLiAMPS chains is negligible compared with the cation mobility. The average mobility of the Li⁺ ions is then determined by the frequency of hopping between sites, which in turn is governed by the residence time of the Li⁺ ions in the vicinity of the anionic sites. The stronger the electrostatic interactions between the cations and the fixed anions, the longer is the average residence time and the smaller is the mobility of lithium ions. The increase in conductivity that results from an increasing proportion of ethylene carbonate in the solvent is consistent with the solvation of cations by ethylene carbonate, which is analogous to the interaction of alkali metal ions with crown ethers. Since solvated lithium ions are not able to approach the anionic sites as closely as non-solvated cations, the anion–cation electrostatic interactions will therefore be weaker, the residence time of the solvated cations in the vicinity of the anions will be reduced, and their hopping frequency will be greater than that of non-solvated cations.

It is, of course, unrealistic to assume that the negative charges on the polyLiAMPS chains are fixed in space. While

translational motion of whole chains is inhibited by the network in which they are imbedded, flexural motions of chain segments should certainly occur. In this case, an additional intermolecular mechanism of lithium ion transport is potentially operative, whereby the flexure of adjacent polyLiAMPS chains creates a pathway for a cation in the vicinity of an anionic site on one of the chains to jump to an equivalent site on the temporarily adjacent chain. This process should also be facilitated by hydration of the cations through weakening the electrostatic interactions by ethylene carbonate.

4. Conclusions

Semi-interpenetrating polyelectrolyte gels formed by linear LiAMPS chains imbedded in cross-linked PMMA have a relatively high conductivity (of the order $0.2\text{--}0.8\text{ mS cm}^{-1}$) at ambient temperature. A feature of these gels is the ability to vary, to a large extent independently, the properties of the network and the concentration of the charge carriers. In this respect, the gels are formally similar to gels made by doping cross-linked PMMA with salts such as lithium triflate and hexafluorophosphate. The advantage of the semi-interpenetrating gel polyelectrolytes is that the translational mobility of the anions is negligible compared with the mobility of the lithium cations.

The dramatic enhancement of conductivity that results from incorporating ethylene carbonate in the solvent implies that ethylene carbonate is implicated in the predominant charge transport mechanisms that are operative in the gels, possibly by solvation of the lithium cations by ethylene carbonate.

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