

Siloxane Diacrylate-based All-Solid Polymer Electrolytes for Lithium Batteries

Matteo Destro, Claudio Gerbaldi, Federico Bella and Jijeesh R. Nair*

Group for Applied Materials and Electrochemistry (GAME Lab), Department of Applied Science and Technology – DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Torino, Italy

Abstract: Fully solid polymer electrolyte (SPE) membranes were prepared by UV induced free radical polymerisation (UV-curing) of acrylated siloxane polyalkyleneoxide copolymers in the presence of different lithium salts. The main chain contains locally mobile segments of ethoxy groups as part of the copolymer, and these moieties can provide coordination sites for the mobility of Li^+ ions. The materials are produced through a solvent free procedure, and used as ion-conducting media as well as a separator in high temperature lithium-based batteries. The preparation process is easy, simple and versatile. The final product obtained demonstrates good mechanical integrity due to the highly cross-linked nature of the polymer network, and wide thermal stability. The membranes are also soft, easy to manage and transparent. They also exhibit acceptable ionic conductivity and wide electrochemical stability window.

Keywords: Siloxane diacrylate, Polymer electrolyte, Ionic conductivity, Photopolymerisation, Lithium battery.

1. INTRODUCTION

Lithium-based batteries have evolved during the years since the discovery by Sony and adapted in many sizes and shapes. This allowed the portable electronics devices to also evolve and perform better. The next step of development is the large-scale penetration of such compact and energy-packed lithium battery systems into the huge market of hybrid-electric and electric vehicles (HEVs-EVs) [1, 2]. It is vital to understand that the further development in the Li-based batteries is related to the investigation of new materials for innovative highly performing electrodes and electrolytes [3]. During these years, the electrolyte systems passed through various systems, trying to move almost completely from all-liquid state to all-solid state or a good compromise in the form of jelly state [4, 5]. However, many voids must be fulfilled to obtain a suitable device.

UV-induced photo-polymerisation (UV-curing) is a widely used polymerisation technique. The whole process takes place under UV light at ambient conditions; the process is fast, economic and most importantly no volatile solvents are used. The basic principle deals with the initiation of a reaction by the decomposition of the light sensitive structure (photo-initiator) to free radicals. These free radicals react further with monomers and oligomers to form a three dimensional network in few minutes. In general, the formulations involve more than one components and

light is the only energy source for the conversion of the reactive mixture to a polymeric thermo-set matrix. The process is industrialised, being economic, fast and environmentally friendly, as the emission of volatile organic matter are negligible [6, 7].

Considering the present scenario and the demand of the various kinds of energy storage devices, it is worth evaluating the possibility of adapting thermoset membranes by free-radical photo-polymerisation (UV-curing) technique as an interesting alternative to the existing methods [7]. Thus, novel siloxane diacrylate oligomer-based all solid state polymer electrolyte membranes were synthesized and their properties were characterised in terms of physical, chemical and electrochemical point of view.

2. MATERIALS AND METHODS

The reactive formulations for the preparation of the solid polymer electrolyte membranes were based on acrylated siloxane polyalkyleneoxide copolymer (SDA, molecular weight 2700 Da, Momentive USA), an acrylic based di-functional oligomer having ethylene oxide moieties. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Ferro Corp. USA), and lithium bisoxalato borate (LiBOB, Chemetall) were used as the source of Li^+ ions, and all of them were battery grade. The free radical photo-initiator was 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173 / D1173), provided by Ciba Specialty Chemicals. Before use SDA was kept open in the inert atmosphere of an Ar-filled dry glove box for several days and also treated with molecular sieves (Molecular sieves, beads 4 Å, 8–12 mesh, Aldrich) to ensure the removal of impurities. In

*Address correspondence to this author at the Group for Applied Materials and Electrochemistry (GAME Lab), Department of Applied Science and Technology – DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129-Torino, Italy; Tel: 0039 011 090 4643; Fax: 0039 011 090 4624; E-mail: jijeesh.nair@polito.it

general, impurities create durability issues and dampen the stability of final rechargeable Li-based battery.

Solid Polymer Electrolyte (SPE) Membrane Preparation

Solid polymer electrolyte (SPE) membranes were prepared as follows: reactive mixtures consisting of various concentrations of siloxane diacrylate (SDA) and various types of lithium salts. 3 wt. % of free radical photo-initiator was always used and added in the last stage of mixing. The exact compositions of the different reactive mixtures and corresponding names of the final membranes are given in Table 1. Once ready, the reactive mixture (SDA:Li salt:Photoinitiator) was deposited over polypropylene (PP) sheets using a calibrated (200 μm) film casting rod. The coated PP sheets were then exposed to UV light for 3 min in two steps, each of 90 s. The polymerisation was carried out under inert atmosphere (N_2 gas) to avoid side reactions involving oxygen. A medium vapour pressure Hg UV lamp purchased from Helios Italquartz (Italy) with a radiation intensity of 40 mW cm^{-2} over the surface of the sample was used as the source of UV irradiation. After the UV irradiation, mechanically stable and self-standing films were detached from the PP support. Overall, the process took less than 5 min for the production of a ready-to-use thin film of solid polymer electrolyte.

Characterization Techniques and Methods

The completion of the polymerisation process was confirmed by gel content studies [5, 9,11]. The gel content was determined by measuring the weight loss of samples contained in metal nets after 18 h of extraction with chloroform. The gel content values listed in Table 1 are calculated with respect to the corresponding SDA content. The thermal stability of the samples was tested between 25 and 600 $^{\circ}\text{C}$ by thermo-gravimetric analysis using a TGA/SDTA-851 instrument (METTLER, Switzerland) under N_2 flux at a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

The ionic conductivity of the SPEs was determined by electrochemical impedance spectroscopy (EIS) between frequency range 100 kHz and 1 Hz at open circuit potential using a PARSTAT-2273 potentiostat instrument. For testing, discs of 2.54 cm^2 (ECC std test cells, EL-CELL GmbH) were cut from the SPE film and sandwiched between two stainless steel (SS-316) blocking electrodes. The assembled cells were kept in a climatic chamber purchased from BINDER GmbH and tested between 20 and 90 $^{\circ}\text{C}$. The resistance of the electrolyte was given by the high frequency intercept determined by analysing the impedance response using a fitting program provided by Princeton Applied Research.

The interfacial properties of the prepared SPE films with the Li metal electrode, and the corresponding variation in resistance with the contact time, were measured by monitoring the time evolution of the impedance (EIS) response of a lithium/SPE/lithium symmetrical cell. The cells were stored at ambient temperature under open circuit conditions.

The anodic breakdown voltage of the SPEs was evaluated by running a sweep voltammetry in a two-electrode ECC-std cell. Acetylene black over Al current collector was used as the working electrode and Li metal as counter and reference electrode, and the given SPE was used as the electrolyte separator. Potential scan range: from O.C.V to 6.0 V vs. Li at a scan rate of 0.100 mVs^{-1} . Under these conditions, the onset of the current at higher potential was assumed as the decomposition potential of the electrolyte [8].

3. RESULTS AND DISCUSSION

The solid polymer electrolyte films prepared by UV-curing of the same formulation described in Table 1 were freestanding, non-tacky, extremely flexible and almost translucent (as shown in the inset of Figure 1). Respective reactive mixtures containing SDA, lithium salt and photo-initiator were UV irradiated for 3

Table 1: The Composition of Various SPEs Prepared by Free Radical Photo-Polymerisation Technique in 3 Minutes and Corresponding Gel Content Values

Name	SDA (wt %)	LITFSI (wt %)	D1173 (wt %)	Gel Content (%)
SDA-10	87	10	3	92
SDA-15	82	15	3	90
SDA-20	77	20	3	85

minutes; photo-polymerisation took place and gave quantitative conversion of the acrylic double bonds.

The overall conversion was checked by gel content analysis. The gel content was always very high (see Table 1), and it was in agreement with the amount of SDA content. It is worth noting that the addition of lithium salt reduced the overall conversion of monomer to polymer. Similar kind of results were obtained with cross-linked methacrylate-based systems [9,10]; they can be related to the presence of charged species in the reaction mixture and related moisture absorption during the sample preparation. Still, the conversion is very high and in all cases exceeded more than 85%, which is a very high value for similar systems cured by UV light [9].

The thermal stability of the polymeric film SDA-10 (representative for all the membranes) was assessed by thermogravimetric analysis (TGA). The corresponding thermogram for SDA-10 (representative for all the samples prepared) is shown in Figure 1. The testing was carried out between 25 and 600 °C under N₂ flow. As expected (siloxane-based polymers are well known for their superior thermal stability [9-11]), the sample showed very high stability, exceeding 300 °C. The initial dip lower than 3% is related to the loss of moisture most likely absorbed during sample preparation. Thus, it can be confirmed that the SPEs prepared using SDA and LiTFSI salt are safe to be used in cells conceived for high temperature applications.

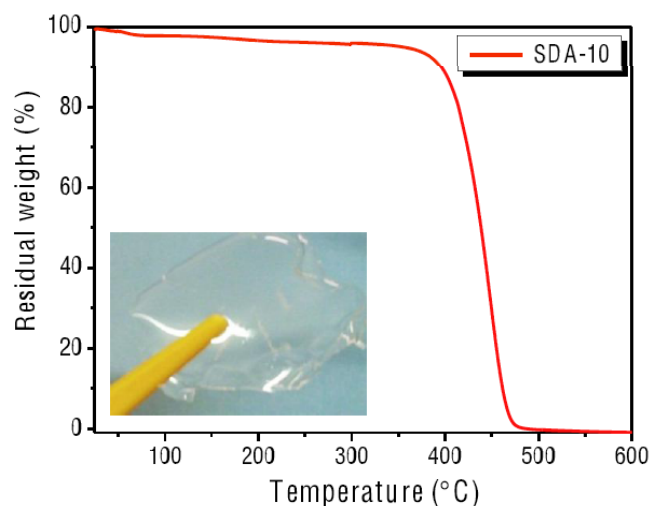


Figure 1: Thermo-gravimetric analysis of SDA-10 membrane between 25 and 600 °C under N₂ flux. Inset: appearance of the SDA-10 membrane obtained via UV-irradiation procedure.

The ionic conductivity of the samples was tested using electrochemical impedance spectroscopy. The Arrhenius plots of the different solid polymer electrolytes are shown in Figure 2 (A and B). The variation in conductivity is linear with the increase in temperature. The ionic conductivity values were found to be reasonably high for a fully solid system. In fact, SDA-15 showed an ambient temperature ionic conductivity of 5×10^{-6} S cm⁻¹. It increased, with increase in temperature, nearing 3×10^{-4} S cm⁻¹ at 90 °C. It was observed that an increase in salt content from 10 wt.% to 15 wt.% increased the ionic conductivity, but a further increase didn't appreciably influence the overall ionic conductivity. Thus, SDA-15 was considered as the ideal material for further characterisation. To study the influence of a non-halogen-based salt, LiBOB was added to the reactive mixture in molar quantity equal to 15 wt.% of LiTFSI content. However, as shown in Figure 2B, it was inferior to SDA-15 membrane. Thus, it was finally decided to test further the electrochemical properties of SDA-15 sample.

In view of its possible application as a polymer electrolyte in lithium batteries, the SDA-15 membrane was further tested in terms of other electrochemical properties, such as oxidation stability towards higher potentials (electrochemical stability window) and reactivity towards lithium metal with time (interfacial stability). LiTFSI based electrolyte was chosen for further studies as it showed higher conductivity values and better solubility characteristics as compared to LiBOB based electrolytes.

The EIS measurements were (shown in Figure 3A) carried out on a Li/SDA-15/Li symmetrical cell. In general, the resistance of a cell is composed of bulk resistance (R_b) of the electrolyte medium and interfacial resistance (R_{ct}) which reflects the compatibility between the electrodes and the electrolyte [9]. The value of R_{ct} slightly increased during the first day, which indicates the formation of a passivating layer on the surface of the lithium metal due to the reactivity of the polymer electrolyte. It subsequently stabilised as showed by the superposition of the curves after 10 and 15 days. Such stabilisation of the interface is the confirmation that the passivation layer is stable and very thin, as the change was not much pronounced. These results match very well with those reported in the literature for similar systems [11].

The stability towards oxidation at higher potentials was evaluated by linear sweep voltammetry at room

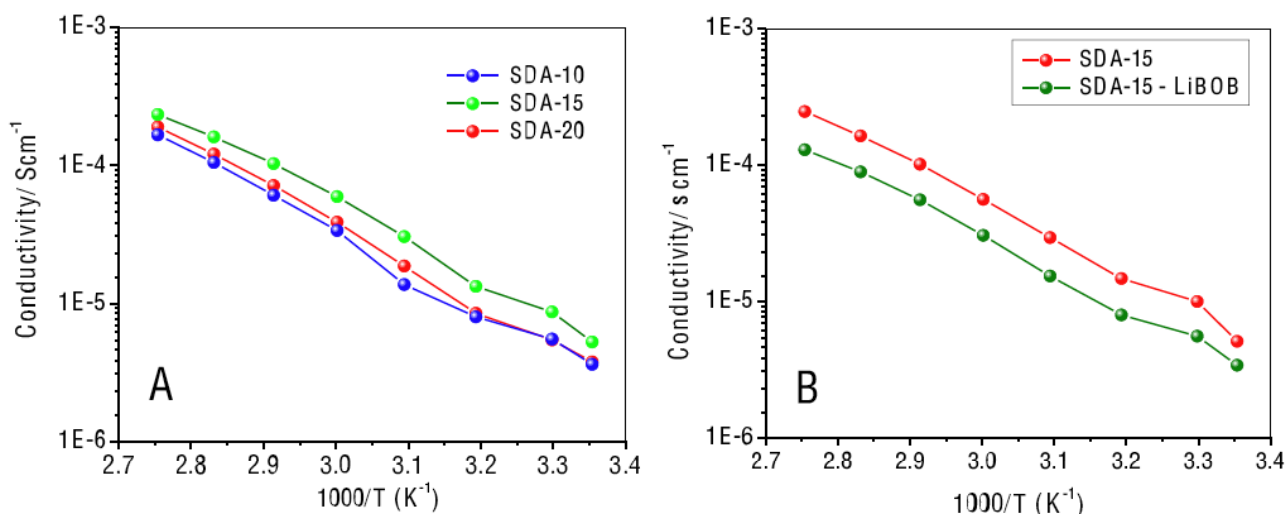


Figure 2: **A)** ionic conductivity vs. temperature plot of the different solid polymer electrolyte membranes; **B)** comparison between ionic conductivity vs. temperature plot of SDA-15 sample with LiBOB salt in equivalent molar ratio corresponding to 15 wt.% of LiTFSI. Data obtained by impedance spectroscopy.

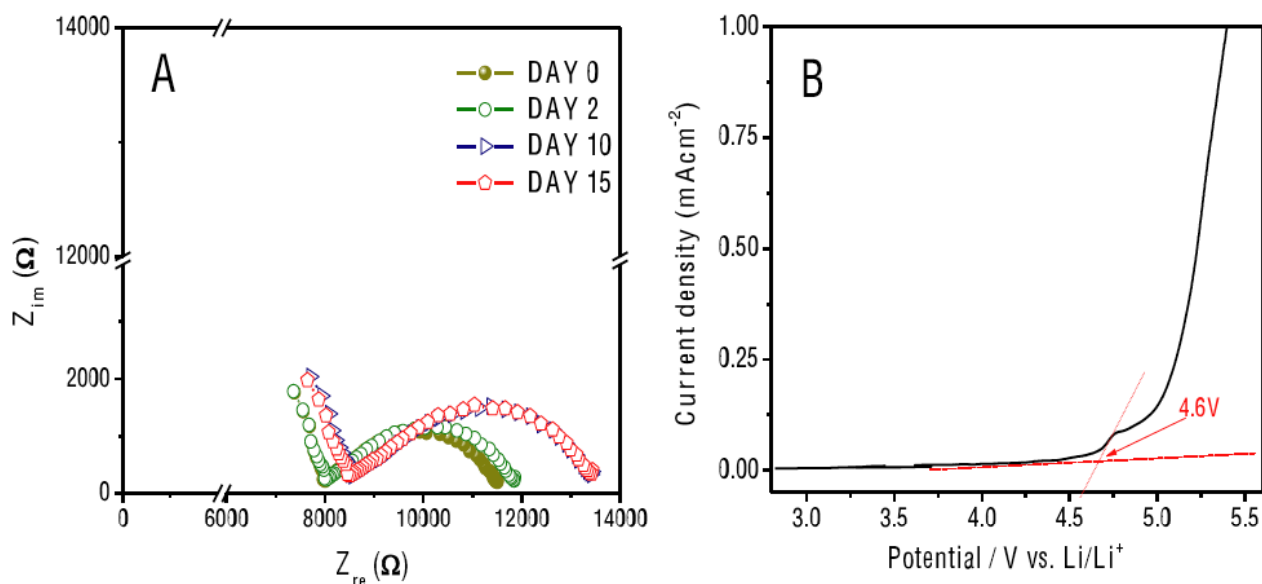


Figure 3: **A)** Nyquist plot representing the evolution of resistance with time for the symmetric cell prepared with Li/SDA-15/Li configuration; **B)** Electrochemical stability window of SDA-15 membrane at room temperature.

temperature. The current–voltage curve, showed in Figure 3B was obtained for a cell assembled with acetylene black over Al as working electrode using the SDA-15 sample as electrolyte and a Li metal as counter and reference electrode. The onset of the current increase indicates the anodic break-down voltage for SDA-15 (4.6V vs. Li/Li⁺), corresponding to the decomposition of some of the electrolyte components. Anodic scan showed very low residual current before reaching the breakdown voltage and such aspect confirms that the membranes prepared are of high purity because lithium battery systems are highly sensitive to oxygen, water and other impurities.

Moreover, a high decomposition potential is promising for high voltage lithium battery applications.

4. CONCLUSION

Fully solid polymer electrolyte membranes were produced using photo-polymerisation procedure and characterised from the physical and electrochemical point of view. The results showed that lithium salt-doped, highly cross-linked siloxane diacrylate based polymer electrolytes can be adapted for high temperature lithium-based rechargeable batteries. Ionic conductivity values exceeding 10⁻⁴ S cm⁻¹ at 70 °C and

electrochemical stability window exceeding 4.6 V vs. Li/Li⁺ are promising features for high temperature applications. Unlike pure PEO-based all solid polymer electrolytes, these UV cured thermoset systems can retain their mechanical integrity even at elevated temperatures, which accounts for the safety aspects of the resulting battery systems. Moreover, UV-curing process is easy to scale up for large quantity applications, economic and environmentally friendly. Further studies are undergoing to investigate the long-term galvanostatic charge/discharge cycling capabilities of such systems in practical lithium metal-based lab scale cells.

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