detritus | Multidisciplinary Journal for Circular Economy and Sustainable Management of Residues

CISA

GEL POLYMER ELECTROLYTES ELABORATED BY UV-IRRADIATION FOR THE ECO-DESIGN OF LI-ION BATTERIES

Ana Barrera [1], Corinne Binet [1], Imene Benabela [2], Philippe Supiot [1], Corinne Foissac [1] and Ulrich Maschke [1,*]

[1] *Unité Matériaux et Transformations (UMET), UMR 8207, CNRS, INRAE, Centrale Lille, Université de Lille, 59000 Lille, France*
[2] *Laboratoire Physico-Chimique des Matériaux, Catalyse et Environnement (LPCMCE), Université des Sciences et de la Technologie Mohammed Boudiaf d'Oran (USTO-MB), 31000 Oran, Algeria*

Article Info:
Received:
29 May 2024
Accepted:
13 July 2024
Available online:
7 September 2024

Keywords:
Gel
Electrolyte
Polymers
Li-ion batteries
UV irradiation
Poly(ethylene glycol) diacrylate

ABSTRACT

This study examines the chemical, thermal, and dielectric properties of gel polymer electrolytes (GPEs) based on poly(ethylene glycol) diacrylate (PEGDA, average M_n=700 g/mol). GPEs were synthesized via a single-step UV-irradiation process, whereby PEGDA was mixed with varying concentrations of a commercial liquid electrolyte (1 M $LiPF_6$ in EC/DEC 50/50 v/v) ranging from 0 to 60 wt%. The results of the infrared analysis indicated that the liquid electrolyte was successfully immobilized within the polymeric matrix. The thermally stable nature of the synthesized GPEs was confirmed across a wide temperature range (-40 to 90°C) through thermal analysis. Furthermore, dielectric measurements were conducted in a frequency range of 0.1 to 10^6 Hz, with a sinusoidal AC amplitude of 10 mV, from 20 to 100°C. The results demonstrated that the ionic conductivity of GPEs increased with the addition of liquid electrolyte. The GPEs prepared with 60 wt% liquid electrolyte exhibited a conductivity value of approximately $6.6x10^{-3}$ S/m at 30°C, which is consistent with the conductivity range reported in the literature.

1. INTRODUCTION

The transition to renewable energies presents a significant challenge in the 21st century, particularly in the area of electrochemical energy storage (Arshad et al., 2020). Lithium-ion batteries (LIBs) have become a crucial component in various applications, including portable electronic devices, industrial equipment, medical devices, and electric vehicles (Grewal et al., 2022; Wang et al., 2021). These accumulators exhibit several advantages over conventional technologies, including lead acid, Ni-Cd, and Ni-metal hybrid batteries. They lack the memory effect, exhibit a low self-discharge rate, possess a high energy density, and can be charged rapidly. Moreover, they exhibit a relatively long lifetime (Raj et al., 2022). Nevertheless, energy storage systems with liquid electrolytes are associated with several disadvantages. These include the risk of explosion or fire, electrolyte leakage, and internal short circuits caused by the formation of lithium dendrites within the anode during charging and discharging (Yao et al., 2019). In response to these concerns, researchers have developed less hazardous alternatives over recent decades. These alternatives seek to replace or adapt the liquid electrolyte with solid materials, including polymers, ceramics, and composites (Maia et al., 2022).

Research on solid polymer electrolytes (SPEs) has primarily focused on polyethylene oxide (PEO) due to its low glass transition temperature (T_g = ~ -60°C) and its ability to effectively complex with Li^+ ions, despite its low dielectric constant (~5) (Mindemark et al., 2018; Q. Zhang et al., 2017). Other polymer families, including acrylates/methacrylates (Kurapati et al., 2019), polynitriles (Arof et al., 2014), fluoropolymers (J. Zhang et al., 2023), polycarbonates (Xu, 2004), and polyesters (Mindemark et al., 2018), have also been the subject of research. Nevertheless, their industrial application remains challenging due to the costly, energy-intensive, and highly sophisticated synthesis techniques required for SPEs. Polymer electrolytes may present certain drawbacks, including low ionic conductivity at room temperature, poor mechanical properties, and limited biodegradability (Zhou et al., 2019). Consequently, it is of paramount importance to develop novel polymer electrolytes that are capable of meeting the demands of LIB applications. The ideal polymer electrolytes would possess excellent mechanical and thermal properties, high ionic conductivity, and enhanced safety.

In recent years, gel polymer electrolytes (GPEs) have emerged as a promising alternative to liquid electrolytes, offering enhanced design versatility and preventing elec-

* Corresponding author:
Ulrich Maschke
email: ulrich.maschke@univ-lille.fr

https://doi.org/10.31025/2611-4135/2024.19406

trolyte leakage (Ren et al., 2021). GPEs trap conventional liquid electrolytes, which are composed of lithium salts dissolved in carbonated organic solvents, within a polymer matrix, thereby reducing the risk of leakage. It is notable that these GPEs serve the dual function of electrolyte and separator, insulating the positive and negative electrodes. This feature significantly reduces the risk of short-circuiting between the electrodes due to the formation of lithium dendrites.

The objective of this study is to examine GPEs, particularly those comprising poly(ethylene glycol) diacrylate (PEGDA), through a single-step synthesis process. The PEGDA will be subjected to UV irradiation in the presence of a photoinitiator. It is generally accepted that UV-light induced polymerization/crosslinking processes enhance the mechanical properties of a GPE. The incorporation of a conventional liquid electrolyte can markedly enhance the conductivity of the polymer electrolyte. The selection of PEGDA was based on its two reactive C=C end bonds and ether functions, which act as electron donors and enhance the ionic conductivity of the synthesized GPEs. Furthermore, the polymer utilized in the synthesis of these GPEs is non-toxic, biodegradable, and exhibits high mechanical strength with a low T_g (Liu et al., 2020). It is also noteworthy that the use of this non-toxic polymer could facilitate the recycling of LIBs.

2. MATERIALS AND METHODS

2.1 Materials

The materials utilized in this study include PEGDA (average M_n=700 g/mol) as a prepolymer, 2-hydroxy-2-methylpropiophenone (Darocur 1173) as a photoinitiator, and a liquid electrolyte (1M $LiPF_6$ in ethyl carbonate/diethyl carbonate (EC/DEC) 50/50 v/v). All of the aforementioned products were procured from Sigma-Aldrich and utilized in their original form.

2.2 Synthesis of gel polymer electrolytes

To elaborate the GPEs, PEGDA and Darocur 1173 (2 wt% related to PEGDA) were combined with varying concentrations of liquid electrolyte, ranging from 0 to 60 wt%. The mixing process was conducted within a glove box, which was maintained under an argon atmosphere, in order to prevent the electrolyte from being exposed to air, which can cause instability. The glove box was maintained at oxygen (O_2) and water (H_2O) levels of less than 0.1 parts per million (ppm). The mixtures were vigorously stirred for four hours, after which polymerization/crosslinking was performed using the ultraviolet irradiation technique.

The liquid mixtures were placed on a Teflon mold in an argon atmosphere and exposed to 365 nm UV light for 30 min, as illustrated in Figure 1a. Following the UV curing process, the samples were placed in an oven maintained at 40°C and 10^{-2} mbar.

The resulting materials are designated as P-X% S, where X represents the weight fraction of liquid electrolyte. Consequently, GPEs manufactured with 20%, 40%, and 60% liquid electrolyte are designated as P-20% S, P-40% S, and P-60% S, respectively. Following the synthesis of the GPEs into disks of approximately 2 cm in diameter and 1 mm in thickness (see Figure 1b), their chemical, thermal, and dielectric properties were characterized. For purposes of comparison, a polymerized/crosslinked PEGDA sample was prepared under similar conditions.

2.3 Chemical, thermal, and dielectric characterizations of GPEs

Fourier transform infrared spectroscopy (FTIR) was employed to monitor the rate of PEGDA polymerization in gel polymer electrolytes (GPEs), the structure of the polymer network, and the impact of lithium salt addition on crosslinking. The measurements were conducted using the attenuated total reflectance (ATR) mode with a diamond prism at wavenumbers ranging from 4000 to 500 cm^{-1} on a Perkin Elmer Frontier spectrometer.

The thermal properties of the GPEs were analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Initially, TGA was employed to ascertain the thermal stability of the samples. The measurements were conducted using a TA Instruments TA Q50 thermogravimetric analyzer under the following experimental conditions: a temperature range of 25 to 800°C, a heating rate of 10°C/min, and a nitrogen gas flow rate of 50 mL/min. The Perkin-Elmer DSC8000 model was employed to ascertain the glass transition temperature (T_g) of GPEs. Samples with masses ranging from 6 to 12 mg were analyzed using a temperature ramp of 10°C/min between -70 and 100°C. To ensure the reliability of the results, three heating and cooling cycles were conducted.

Dielectric spectroscopy was employed to quantify the ionic conductivity of GPE. The measurements were conducted using a ModuLab-MTS impedancemeter (Solartron Analytical) with a sinusoidal AC voltage amplitude of 10 mV in the frequency range of 0.1 to 10^6 Hz at temperatures ranging from 20 to 100°C. Temperature studies were conducted using a Prolabo oven, which is a standard labora-

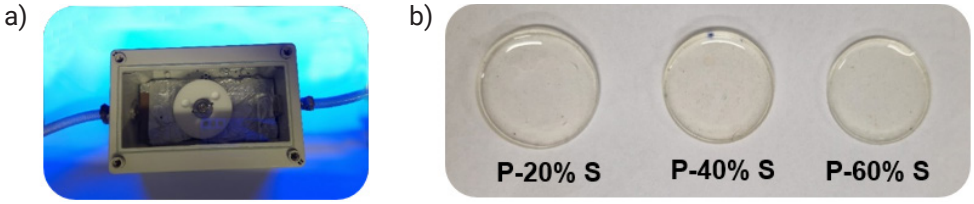

FIGURE 1: a) Teflon mold placed in an argon atmosphere for the UV-irradiation process, b) synthetized GPEs as disks measuring approximately 2 cm in diameter and 1 mm in thickness (P-20 %S, P-40% S and P-60% S).

tory apparatus. The experiments were conducted using a custom-built Swagelok apparatus. The device comprises two stainless-steel electrodes in contact with the sample on both sides and supported by a spring system. Conductivity values were determined from the Nyquist plot, which is obtained by plotting the imaginary (-Z") and real (Z') parts of the complex impedance (Z*). A fit was performed on the resulting semicircle to obtain the resistance (R), which is related to Z', and equation (1) was used to calculate the conductivity of the GPEs.

$$\sigma' = d/RS \quad (1)$$

where σ' is the electrical conductivity (S/m), d stands for the sample thickness (m), R represents the apparent resistance (Ω), and S corresponds to the sample surface area (m²).

3. RESULTS AND DISCUSSION

3.1 Chemical properties

Figure 2 depicts the Fourier transform infrared (FTIR) spectra of PEGDA before and after ultraviolet (UV) irradiation, with the addition of 20, 40, and 60 weight percent (wt%) of the liquid electrolyte, which forms the gel polymer electrolytes (GPEs; P-20% S, P-40% S, and P-60% S), as well as the pure liquid electrolyte. The PEGDA prepolymer spectrum exhibits characteristic bands at 1410 and 810 cm^{-1}, which are attributed to the acrylic double bonds -CH=CH-. The disappearance of these bands after exposure to UV light indicates that the acrylic functions have undergone complete conversion, resulting in the formation of a crosslinked polymer matrix.

In the spectra of the GPE samples (P-20% S, P-40% S, and P-60% S), new bands appear around 1780 and 1830 cm^{-1}, corresponding to the carbonate groups (C=O) present in the organic solvents ethyl carbonate (EC) and diethyl carbonate (DEC). This evidence corroborates the presence of a liquid electrolyte within the matrix.

Furthermore, peaks at 840 and 550 cm^{-1} are observed, which are attributed to the vibrational mode (t_{1u}) of $[PF_6]^-$ present in the lithium salt, thereby confirming its presence in GPEs (Xuan et al., 2005). It is notable that the PEGDA polymer matrix was selected for the synthesis of these GPEs due to the presence of polar carbonyl and ether groups, which act as electron donors (Liu et al., 2020). The coordination of Li^+ ions with the oxygen atoms present in these groups has the potential to enhance the ionic conductivities of GPEs.

3.2 Thermal characterization

Figure 3 depicts the thermograms obtained from the TGA analysis of polymerized/crosslinked PEGDA, GPEs with varying liquid electrolyte contents, and liquid electrolyte. The PEGDA polymer exhibited a single degradation step with an onset degradation temperature of approximately 350°C. In contrast, the pure liquid electrolyte is comprised of three distinct phenomena: (i) thermal degradation of $LiPF_6$ in electrolyte solution below 100°C, (ii) evaporation of DEC near its boiling point (130°C), and (iii) evaporation of EC at 250°C. Additionally, several degradation processes were identified for the GPE samples, including thermal decomposition of $LiPF_6$ and solvent evaporation below 250°C. The weight loss percentages indicate that the rate of solvent evaporation is slower in the GPEs than in the electrolyte. This effect becomes more pronounced as the percentage of electrolyte in the mixture decreases. Furthermore, the lithium salt in the GPEs tends to dissociate at low temperatures. The final degradation step occurred at approximately 300°C and was attributed to the degradation of crosslinked PEGDA. This indicated a loss of thermal stability in comparison to the pure PEGDA polymer. At the conclusion of the analysis at 800°C, approximately 8% of the mass of the GPE sample remained. This residue may be indicative of the formation of carbon residues during analysis under a nitrogen (N_2) atmosphere. The technical specifications for LIBs require

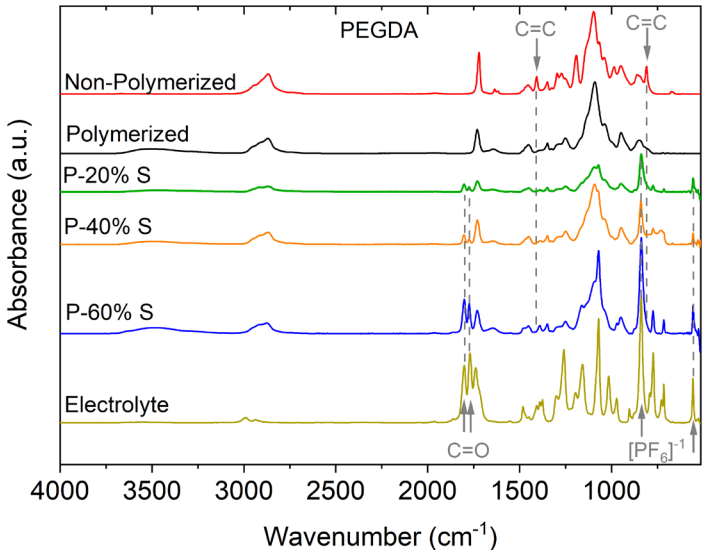

FIGURE 2: FTIR spectra of pristine PEGDA before and after polymerization/crosslinking, P-20 %S, P-40% S, P-60% S, and the pure liquid electrolyte.

a thermal stability range of -20 to 60°C. Our GPEs meet this requirement, as they are thermally stable up to at least 90°C.

Figure 4 displays the DSC curves for the PEGDA polymer and GPEs with varying liquid electrolyte concentrations.

Figure 4 illustrates that each sample exhibits a single T_g. This T_g represents the minimum temperature at which the GPEs can be effectively utilized for an application in LIBs. The T_g of PEGDA polymer is approximately -42°C, and the addition of a liquid electrolyte results in a slight shift in T_g values toward lower temperatures. As previously stated, the optimal operational temperatures for a LIB are between -20 and 60°C, in accordance with its specifications. Given that all the GPEs synthesized in this study have T_g values above -40°C, they are suitable for use in LIBs.

3.3 Dielectric characterization

The ionic conductivity of GPEs is a crucial property for their utilization in LIBs. Consequently, as previously stated, dielectric studies are of paramount importance in order to ascertain the conductivity values of GPEs. Figure 5a and b display Nyquist plots for PEGDA polymer and GPE synthesized with 20 wt% of liquid electrolyte (P-20% S), respectively, over a temperature range from 20 to 100°C.

The conductivity was calculated using Equation (1) based on the resistance measured on the circular part of the curves, as previously mentioned. Figure 5 indicates that the polymerized/crosslinked PEGDA sample exhibits higher resistance values than the GPE sample with 20 wt% liquid electrolyte, resulting in lower conductivities. Specifically, at 20°C, the ionic conductivity of the PEGDA polymer

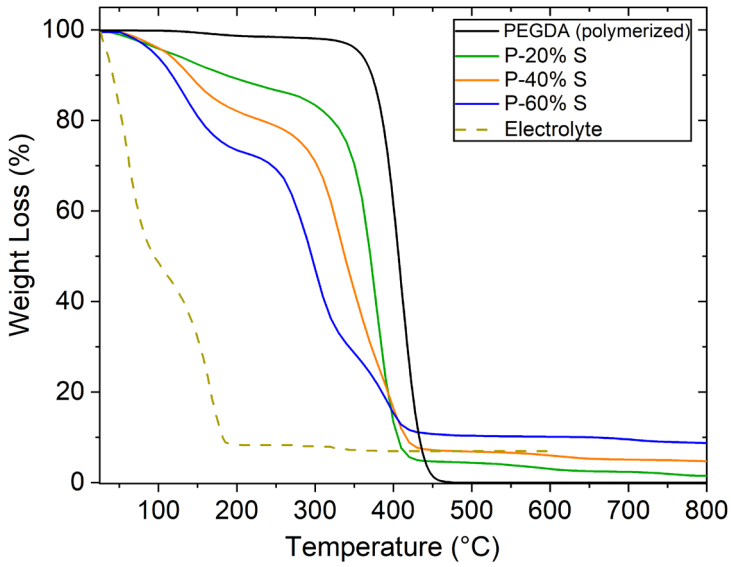

FIGURE 3: TGA curves of polymerized/crosslinked PEGDA, P-20 %S, P-40% S, P-60% S, and liquid electrolyte. Data for the liquid electrolyte were extracted from (Netzsch, 2019).

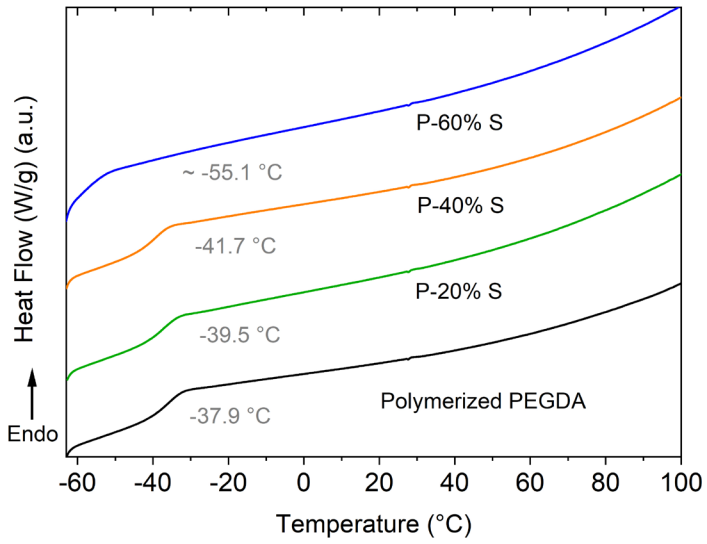

FIGURE 4: DSC thermograms of polymerized/crosslinked PEGDA, P-20% S, P-40% S, and P-60% S in the temperature range of -70°C to 100°C at a rate of 10°C/min. The temperatures indicated in the figure correspond to the glass transition.

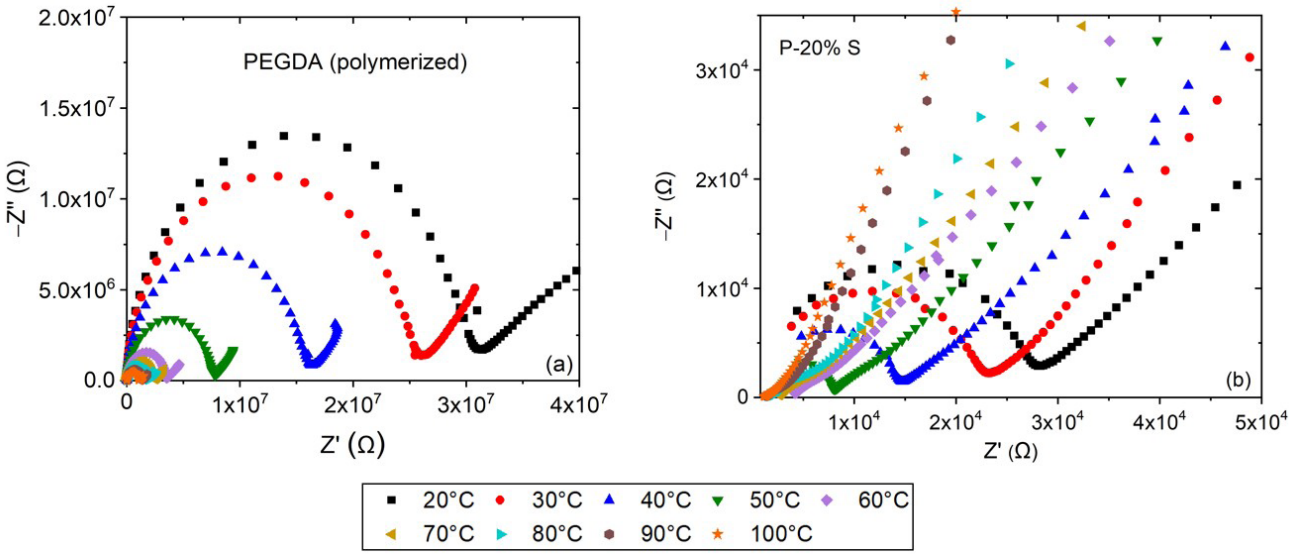

FIGURE 5: Nyquist plots of (a) polymerized/crosslinked PEGDA and (b) GPE synthesized with 20 wt% of liquid electrolyte (P-20% S), respectively. The measurements were conducted over a temperature range of 20 to 100°C.

is $3.6x10^{-6}$ S/m, while that of the GPE (P-20% S) is $3.4x10^{-4}$ S/m, representing a two-decade increase. Moreover, it has been observed that an increase in temperature results in a reduction in the radius of the circular portion of the Nyquist plots, which in turn leads to an increase in the conductivity values of the samples. At a temperature of 100°C, the conductivity value of GPE is $1.1x10^{-2}$ S/m, which is two orders of magnitude higher than the conductivity value at 20°C. This is attributed to the enhanced mobility of charge carriers and the facilitated movement of polymer chains within the network.

Figure 6 presents a summary of the evolution of ionic conductivity with temperature and liquid electrolyte concentration. The conductivity values increase with rising temperature and liquid electrolyte concentration in the synthesized GPEs. The sample with a 60 wt% liquid electrolyte concentration (P-60% S) exhibited the highest conductivity values among the other GPEs, with a value of $6.6x10^{-3}$ S/m at 30°C. The reported conductivity is comparable to that of traditional liquid electrolytes, which range from approximately 10^{-3} to 1 S/m (Liu et al., 2020; Mindemark et al., 2018; Zhou et al., 2019).

The temperature dependence of the ionic conductivities of polymerized/crosslinked PEGDA and synthesized GPEs was analyzed using the Arrhenius law. Figure 6 illustrates that all samples exhibited Arrhenius-type behavior within the temperature range of 20 to 100°C. The activation energies (E_a) were determined to be 0.44, 0.42, and 0.38 eV for the P-20% S, P-40% S, and P-60% S GPEs, respectively, by fitting the experimental data. These activation energies exhibit a slight increase with increasing polymer content and fall within the typical range of those reported for GPEs

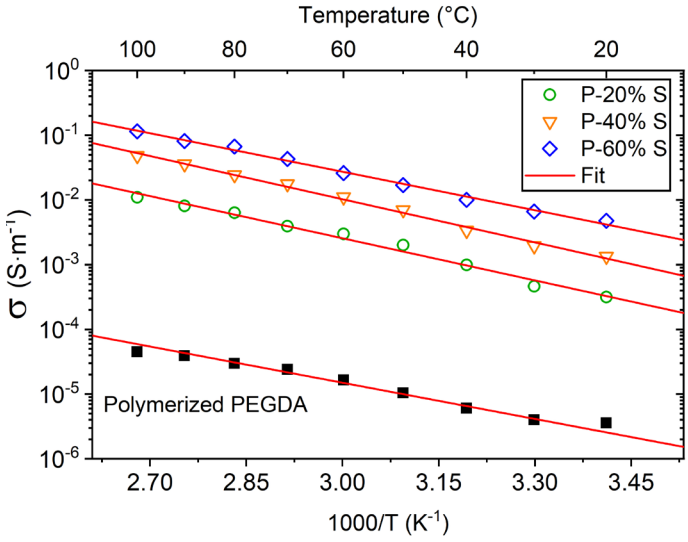

FIGURE 6: Conductivity measurements of polymerized/crosslinked PEGDA, P-20% S, P-40% S, and P-60% S at varying temperatures. The solid red lines represent data analysis conducted in accordance with the Arrhenius law.

synthesized elsewhere (D'Angelo & Panzer, 2017; Shalu et al., 2013).

4. CONCLUSIONS

In this study, PEGDA-based GPEs with varying concentrations of $LiPF_6$ dissolved in carbonated organic solvents were successfully synthesized via ultraviolet (UV) irradiation. Infrared spectroscopy demonstrated that the liquid electrolyte was confined within the polymer matrix. Thermal analysis demonstrated that all synthesized GPEs exhibited thermal stability within a temperature range of -40°C to 90°C, which is higher than the conventional temperature range of -20°C to 60°C typically observed for LIBs. Dielectric measurements demonstrated that the ionic conductivity of the GPEs increased with increasing temperature and liquid electrolyte concentration. The GPE with 60 wt% liquid electrolyte (P-60% S) exhibited the highest ionic conductivity among the samples, with a value of 6.6 x 10^{-3} (S/m) at 30°C. The ionic conductivity is comparable to that reported in the literature for electrolyte polymers. The aforementioned properties indicate that the GPEs prepared via the one-step method may be suitable as electrolytes in LIBs.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by the University of Lille and the Région Hauts-de-France.

REFERENCES

Arof, A. K., Amirudin, S., Yusof, S. Z., & Noor, I. M. (2014). A method based on impedance spectroscopy to determine transport properties of polymer electrolytes. Physical Chemistry Chemical Physics, 16(5), 1856–1867. https://doi.org/10.1039/c3cp53830c

Arshad, F., Li, L., Amin, K., Fan, E., Manurkar, N., Ahmad, A., Yang, J., Wu, F., & Chen, R. (2020). A Comprehensive Review of the Advancement in Recycling the Anode and Electrolyte from Spent Lithium Ion Batteries. ACS Sustainable Chemistry and Engineering, 8(36), 13527–13554. https://doi.org/10.1021/acssuschemeng.0c04940

D'Angelo, A. J., & Panzer, M. J. (2017). Enhanced Lithium Ion Transport in Poly(ethylene glycol) Diacrylate-Supported Solvate Ionogel Electrolytes via Chemically Cross-linked Ethylene Oxide Pathways. Journal of Physical Chemistry B, 121(4), 890–895. https://doi.org/10.1021/acs.jpcb.6b10125

Grewal, M. S., Kisu, K., Orimo, S. ichi, & Yabu, H. (2022). Increasing the ionic conductivity and lithium-ion transport of photo-cross-linked polymer with hexagonal arranged porous film hybrids. IScience, 25(9), 104910. https://doi.org/10.1016/j.isci.2022.104910

Kurapati, S., Gunturi, S. S., Nadella, K. J., & Erothu, H. (2019). Novel solid polymer electrolyte based on PMMA:CH_3COOLi effect of salt concentration on optical and conductivity studies. Polymer Bulletin, 76(10), 5463–5481. https://doi.org/10.1007/s00289-018-2659-5

Liu, M., Wang, Y., Li, M., Li, G., Li, B., Zhang, S., Ming, H., Qiu, J., Chen, J., & Zhao, P. (2020). A new composite gel polymer electrolyte based on matrix of PEGDA with high ionic conductivity for lithium-ion batteries. Electrochimica Acta, 354, 136622. https://doi.org/10.1016/j.electacta.2020.136622

Maia, B. A., Magalhães, N., Cunha, E., Braga, M. H., Santos, R. M., & Correia, N. (2022). Designing Versatile Polymers for Lithium-Ion Battery Applications: A Review. Polymers, 14(3). https://doi.org/10.3390/polym14030403

Mindemark, J., Lacey, M. J., Bowden, T., & Brandell, D. (2018). Beyond PEO—Alternative host materials for Li+-conducting solid polymer electrolytes. Progress in Polymer Science, 81, 114–143. https://doi.org/10.1016/j.progpolymsci.2017.12.004

Netzsch. (2019). Thermal Stability of Lithium Ion Battery Electrolyte. https://analyzing-testing.netzsch.com/fr/application-literature/thermal-stability-of-lithium-ion-battery-electrolyte

Raj, T., Chandrasekhar, K., Kumar, A. N., Sharma, P., Pandey, A., Jang, M., Jeon, B. H., Varjani, S., & Kim, S. H. (2022). Recycling of cathode material from spent lithium-ion batteries: Challenges and future perspectives. Journal of Hazardous Materials, 429, 128312. https://doi.org/10.1016/j.jhazmat.2022.128312

Ren, W., Ding, C., Fu, X., & Huang, Y. (2021). Advanced gel polymer electrolytes for safe and durable lithium metal batteries: Challenges, strategies, and perspectives. Energy Storage Materials, 34, 515–535. https://doi.org/10.1016/j.ensm.2020.10.018

Shalu, Chaurasia, S. K., Singh, R. K., & Chandra, S. (2013). Thermal stability, complexing behavior, and ionic transport of polymeric gel membranes based on polymer PVdF-HFP and ionic liquid, [BMIM][BF_4]. Journal of Physical Chemistry B, 117(3), 897–906. https://doi.org/10.1021/jp307694q

Wang, Z., Shen, L., Deng, S., Cui, P., & Yao, X. (2021). 10 μm-Thick High-Strength Solid Polymer Electrolytes with Excellent Interface Compatibility for Flexible All-Solid-State Lithium-Metal Batteries. Advanced Materials, 33(25), 1–7. https://doi.org/10.1002/adma.202100353

Xu, K. (2004). Nonaqueous liquid electrolytes for lithium-based rechargeable batteries. Chemical Reviews, 104(10), 4303–4417. https://doi.org/10.1021/cr030203g

Xuan, X., Wang, J., & Wang, H. (2005). Theoretical insights into PF_6^- and its alkali metal ion pairs: Geometries and vibrational frequencies. Electrochimica Acta, 50(20), 4196–4201. https://doi.org/10.1016/j.electacta.2005.01.045

Yao, P., Yu, H., Ding, Z., Liu, Y., Lu, J., Lavorgna, M., Wu, J., & Liu, X. (2019). Review on Polymer-Based Composite Electrolytes for Lithium Batteries. Frontiers in Chemistry, 7, 1–17. https://doi.org/10.3389/fchem.2019.00522

Zhang, J., Zeng, Y., Li, Q., Tang, Z., Sun, D., Huang, D., Zhao, L., Tang, Y., & Wang, H. (2023). Polymer-in-salt electrolyte enables ultrahigh ionic conductivity for advanced solid-state lithium metal batteries. Energy Storage Materials, 54, 440–449. https://doi.org/10.1016/j.ensm.2022.10.055

Zhang, Q., Liu, K., Ding, F., & Liu, X. (2017). Recent advances in solid polymer electrolytes for lithium batteries. Nano Research, 10(12), 4139–4174. https://doi.org/10.1007/s12274-017-1763-4

Zhou, D., Shanmukaraj, D., Tkacheva, A., Armand, M., & Wang, G. (2019). Polymer Electrolytes for Lithium-Based Batteries: Advances and Prospects. Chem, 5(9), 2326–2352. https://doi.org/10.1016/j.chempr.2019.05.009