



Journal of Functional Materials and Biomolecules

Journal homepage: www.shcpub.edu.in



ISSN: 2456-9429

CHARACTERIZATION OF PROTON CONDUCTING LIQUID ELECTROLYTE BASED ON LOW MOLECULAR WEIGHT POLYETHYLENE GLYCOL₂₀₀ - AMMONIUM THIOCYANATE

Daries Bella. R. S^{1*}, Marian Kirthena P.C¹, R.S. Diana Sangeetha²

Received on 28 November 2023, accepted on 5 December 2023,
Published online on November 2023

Abstract

Liquid electrolytes were prepared using PEG₂₀₀ as host polymer and NH₄SCN as ionic dopant with different concentration. The prepared liquid electrolytes were characterized by UV-VIS, FTIR, and ac impedance spectroscopic techniques. Transmittance of the electrolytes can be controlled by ionic dopant especially at UV wavelength region. Complex nature of liquid electrolytes is confirmed by FTIR analysis. DC conductivity of the liquid electrolyte is calculated as 0.32 mS/cm for 0.25g NH₄SCN added system. It is also observed that dc conductivity mechanism dominates for all liquid electrolytes.

Keywords: PEG₂₀₀, NH₄SCN, liquid electrolytes, ac impedance analysis.

1. Introduction

A number of batteries with H⁺, Li⁺ and Na⁺ ions were developed. Many studies were reported on Li⁺ based batteries because of the availability of good lithium ion conductors and large electrochemical stability window [1-4]. High cost and difficulty in handling lithium electrodes are few problems associated with Li⁺ based batteries. Proton batteries in spite of its low electrochemical stability window can be considered as alternative to Li⁺ - based batteries in view of its cost effectiveness [5]. Many attempts have already been made to develop proton batteries using liquid electrolytes as well as polymer electrolytes because of its attractive features such as:

- ❖ Ease of fabrication
- ❖ Safe
- ❖ Less expensive
- ❖ Environmentally friendly

One of the important advantages of using liquid electrolyte is higher electrode-electrolyte contact area than other solid or polymer electrolytes. Liquid electrolyte also plays the role of conducting proton ions through it and not allowing electrons to flow. It is important to prepare the electrolyte that shows higher ionic conductivity and good electrochemical window. PEG is one of the polymers which occur in liquid state at low molecular weight [6-8]. PEG₂₀₀, PEG₄₀₀, PEG₆₀₀ are appeared in liquid state. Ethylene group cause the dissolution of salt and creates ions.

NH₄SCN is a proton donor and supply NH₄⁺ to the electrolyte [9-12]. In the present work, it is proposed to synthesis liquid electrolytes based on PEG₂₀₀ and NH₄SCN with different ratio. These electrolytes will be subjected to conductivity studies to find its suitability in proton battery applications.

2. Experimental procedure

2.1. Materials and preparation of electrolytes

Liquid electrolytes were prepared basically using solvent and solute. The Solvent host (Polyethylene Glycol 200) of 20 ml and salt (NH₄SCN) with different concentration were taken and mixed gently together using the magnetic stirrer. The mixture was stirred continuously using magnetic stirrer and made the mixture to be homogenous Solution, by this process Liquid electrolyte is formed. The following flowchart shows the preparation of liquid electrolytes.

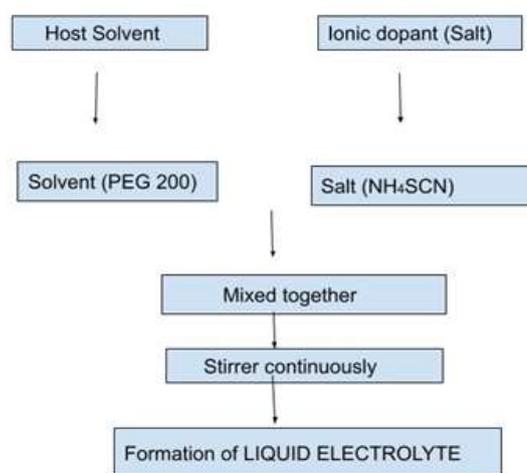


Figure: 1 Flowchart for the Preparation of Liquid Electrolytes by the solution method

*Corresponding author email: dariesbella@stellamariscollege.edu.in

¹ Department of Physics, Stella Maris College (Autonomous), Chennai, India.

² Department of Chemistry, Sacred Heart College (Autonomous), Tirupattur, Vellore, India

2.2 Nomenclature

Table 1. Details on weight of the salt and nomenclature.

S.No	Solute	Solvent	Nomenclature
1	NH ₄ SCN:0.05g	PEG ₂₀₀ (20ml)	NS0.05
2	NH ₄ SCN:0.1g	PEG ₂₀₀ (20ml)	NS0.1
3	NH ₄ SCN:0.15g	PEG ₂₀₀ (20ml)	NS0.15
4	NH ₄ SCN:0.2g	PEG ₂₀₀ (20ml)	NS0.2
5	NH ₄ SCN:0.25g	PEG ₂₀₀ (20ml)	NS0.25
6	NH ₄ SCN	-	NS
7	-	PEG ₂₀₀	PEG ₂₀₀

The nomenclature and weight of salt are given in the above table.

2.3. Characterization techniques

FTIR spectra were recorded for the liquid electrolyte using JASCO FTIR-4100 spectrometer in the wave number range of 400 cm⁻¹ - 4000 cm⁻¹. UV-Visible spectra were recorded by using JASCO V-730 spectrophotometer in the range of 190 nm – 900 nm at room temperature. The ac impedance studies of the liquid electrolytes were carried out by using electro chemical analyser model CH608E with two probe method.

3. Result and Discussion

3.1 FTIR analysis of PEG₂₀₀ and NH₄SCN liquid electrolytes:

FTIR spectroscopic technique has been used to analyse the interaction among ions in the liquid electrolyte system. The figure 2 shows the FTIR spectra for the samples PEG₂₀₀, NS, NS 0.05, NS 0.1, NS 0.15, NS 0.2, and NS 0.25. Various important vibrational band assignments are given in the table 2.

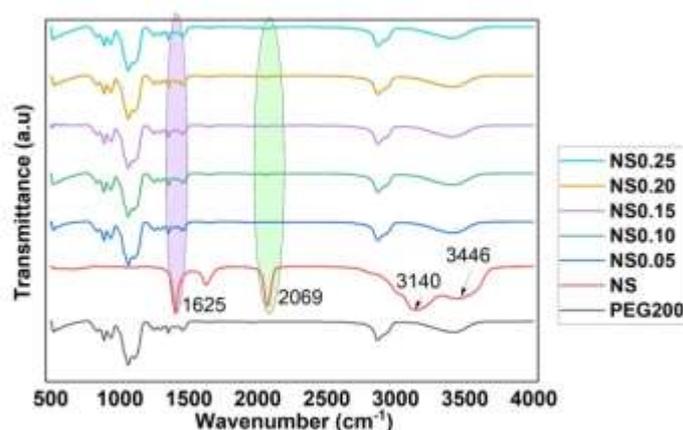


Figure: 2 FTIR spectra for PEG₂₀₀ and NH₄SCN based liquid electrolytes

Table: 2 Few important vibrational bands of liquid complex

Wave number (cm ⁻¹)	Assignments
1400	NH Deformation
1625	SCN asymmetric stretching vibration
2069	SCN asymmetric stretching vibration
3140	N-H Stretching
3446	O-H Vibration

As the concentration of the salt in solution increases, the shift in the vibrational bands are observed. The band around 1400 cm⁻¹ and 2069 cm⁻¹ are assigned to deformation of NH bending and SCN asymmetric stretching vibration respectively of pure NH₄SCN. When the salt concentration increases, these peaks are shifted to lower wavenumber side due to the interaction of PEG₂₀₀. The band around 3446 cm⁻¹ are ascribed to O-H stretching vibration of pure poly ethylene glycol. This band gets broadened on addition of salt. These changes in the wave number upon addition of salt confirm the complex nature of the liquid electrolytes.

3.2 UV-Vis analysis of PEG₂₀₀ and NH₄SCN liquid electrolytes:

The figure 3 shows that the transmittance peaks for the pure PEG₂₀₀ and different concentration of NH₄SCN in the range of 190 nm – 900 nm. Pure PEG shows

absorption band at 205 nm and the absorbance of the liquid electrolytes begins at 250 nm. Upon the addition of salt concentration, new peak is found and this peak is gradually shifted in the liquid electrolytes. It is further observed that pure PEG200 shows 90% transmittance up to 250 nm and maximum transmittance gets reduced at lower wavenumber region on addition of salt. It is confirmed that transmittance of pure PEG200 can be controlled by the addition of salt at UV region.

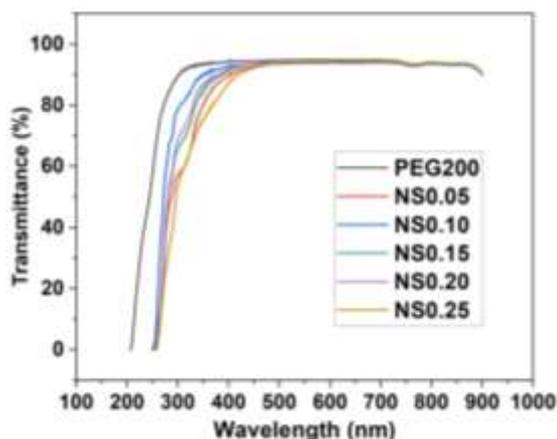


Figure: 3 Transmittance spectra of PEG₂₀₀ - NH₄SCN based liquid electrolytes

3.3. AC impedance analysis of PEG₂₀₀ and NH₄SCN liquid electrolytes:

According to Almond and West [13] the frequency dependence of ac conductivity of polymer complex is described by the following equation,

$$\sigma_{ac} = \sigma_{dc} + A \omega^n \dots \dots \dots 1$$

where A and n are material parameters, $0 < n < 1$. σ_{dc} is the dc conductivity and ω is angular frequency. The variation of $\log \sigma_{ac}$ with $\log \omega$ for the liquid electrolyte system with different concentration of NH₄SCN at room temperature is shown in Figure 4. From the plot, it is

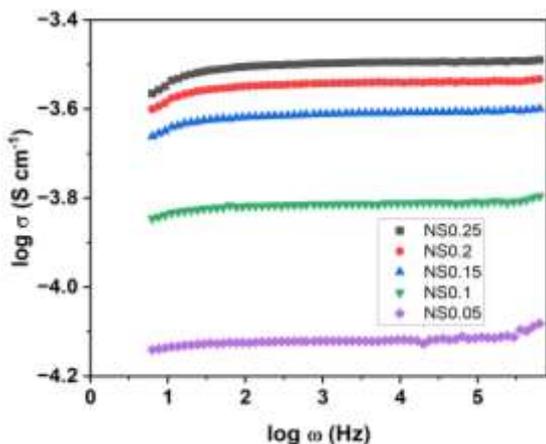


Figure: 4 Conductance spectra of PEG₂₀₀ - NH₄SCN based liquid

-electrolyte observed that the curve consists of three different regions; the low frequency dispersion which is followed by the medium frequency plateau and a spike at high frequencies.

Table 3: DC conductivity of PEG₂₀₀-NH₄SCN liquid electrolytes

Samples	Dc conductivity (mS/cm)
NS0.05	7.574×10^{-2}
NS0.1	$1.54. \times 10^{-1}$
NS0.15	$2.47. \times 10^{-1}$
NS0.2	2.89×10^{-1}
NS0.25	3.21×10^{-1}

The high frequency part of the curve corresponds to bulk relaxation phenomena, whereas the plateau region is connected with the dc conductivity (σ_{dc}) of the liquid electrolytes. The low frequency dispersion describes the electrode – electrolyte interfacial phenomena or space charge polarization.

As the frequency decreases, more and more charge accumulation occurs at the electrode and electrolyte interface, which leads to a decrease in number of mobile ions and eventually to a drop in conductivity at low frequency. In high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency. DC conductivity is calculated by extrapolating the dc plateau region to the y-axis. It is found that the dc conductivity is greater for 0.25 g of NH₄SCN in liquid electrolyte and the dc conductivity of all electrolytes is given in the table 3.

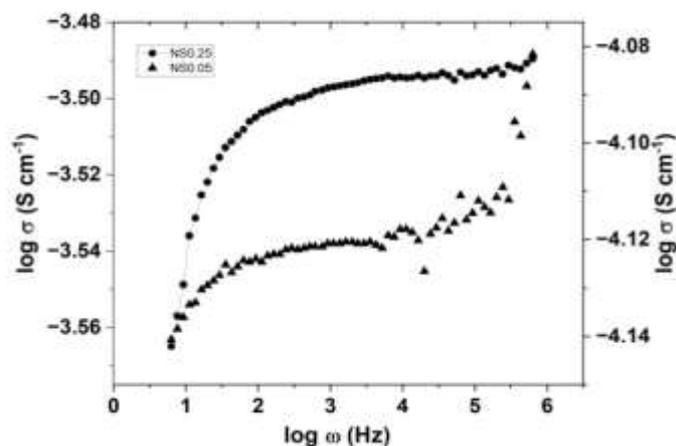


Figure: 5 ac conductance spectra of NS0.05 and NS0.25 of liquid electrolytes

Figure 5 shows the ac conductance spectre of lower and higher concentration of NH_4SCN in PEG_{200} . In this figure clearly shows the three different region in ac conductance spectra. Almond and West formalism can be fitted in high frequency region and 'n' value can also be extracted.

The complex dielectric permittivity ' ϵ^* ' can be calculated by

$$\epsilon^* = \epsilon' + i\epsilon'' \quad \dots\dots\dots 2$$

where ϵ' is the real (relative permittivity or dielectric constant) and ϵ'' is the imaginary (dielectric loss) parts of the complex dielectric permittivity.

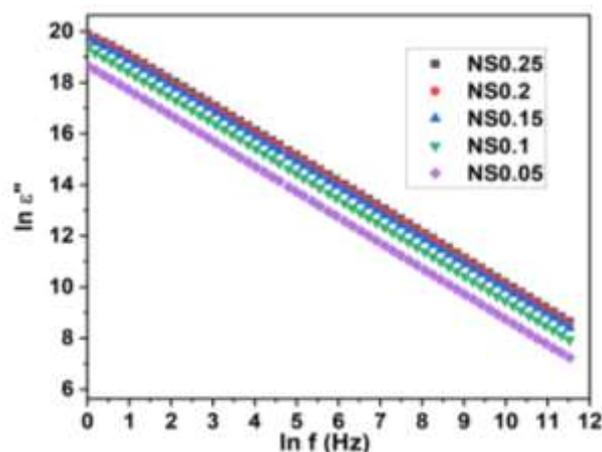


Figure: 6 Variation of dielectric loss for PEG_{200} – NH_4SCN liquid electrolytes

The dielectric permittivity analysis provides information on the transport properties of ions in the electrolyte. The real part of the permittivity measures the alignment of dipoles and the imaginary part represents the energy required to align the dipoles and to move ions.

Table: 4 Power law exponent value for PEG_{200} – NH_4SCN liquid electrolytes

Samples	(n-1) value
NS0.05	-1
NS0.1	-0.99999
NS0.15	-0.99998
NS0.2	-0.99996
NS0.25	-0.99994

Figure 6 shows the variation of $\log \epsilon''$ with respect to $\log \omega$ for NS0.00, NS0.05, NS0.1, NS0.15, NS0.2 and NS0.25 respectively. All spectra have been fitted by linear straight line fit with regression of 0.999. The frequency

dependent dielectric losses (ϵ'') are proportional to ω^{n-1} in the frequency region studied and 'n' is power law exponent. The exponent, (n-1) tends towards "-1" as shown in the table 4. It clearly shows that the dc conductivity dominates in these types of liquid electrolytes [13-17].

4. Conclusion

The liquid electrolytes have been prepared with PEG_{200} as host and NS_4SCN as dopant with different dopant concentration. From UV-VIS analysis, the transmittance of PEG_{200} can be controlled by addition of salt especially at UV region. Complex nature of liquid electrolytes are confirmed by FTIR analysis. The dc conductivity of liquid electrolytes increases upon salt concentration increases. From the dielectric spectra, it clearly confirms that the dc conductivity dominates in these types of liquid electrolytes.

Reference

- [1] Chandra S. (Ed.), *Superionic solids – Principles and Applications*, North Holland, Amsterdam (1981).
- [2] Munshi M. Z. A. (Ed.), *Handbook of Solid state Batteries and capacitors*, World Scientific, Singapore (1995).
- [3] Dion Hubble, David Emory Brown, Yangzhi Zhao, Chen Fang, Jonathan Lau, Bryan D. McCloskey and Gao Liu, *Energy & Environmental Science*, 2, (2022)
- [4] Hansen Wang, Zhiao Yu, Xian Kong, Sang Chol Kim, David T. Boyle, Jian Qin, Zhenan Bao, Yi Cui, *Joule*, 6(3), 588-616 (2022)
- [5] Guitton J., B.Dongui, R.Mosdale, M.Forestier, *Solid State Ionics*, 28-30, 847-852 (1988).
- [6] LingzhuZhao, Jingchuan Fu, ZhiDU, Xiaobojia, YanyuQu, FengYu, JieDu, YongChen *Journal of Membrane Science*, 593, 117428 (2020)
- [7] Jin HyokRi, JingpengJin, JinleiXu, TianyouPeng, Kwon IlRyu, *Electrochimica Acta*, 201, 251-259 (2016)
- [8] Xuejing Zhang, Xingchao Wang, Shuang Liu, Zhanliang Tao, Jun Chen, *Nano Research*, 11, 6244-6251 (2018).
- [9] N.A.Shamsuri, S. N. A. Zaine, Y. M. Yusof, W. Z. N. Yahya, M. F. Shukur, *Ionics*, 26, 6083-6093 (2020)
- [10] M. F. Z. Kadir, M. H. Hamsan, *Ionics*, 24, 2379-2398 (2018)
- [11] R.Hemalatha, M.Alagar, S.Selvasekarapandian, B.Sundaresan, V.Moniha, *Journal of Science: Advanced Materials and Devices*, 4(1), 101-110 (2019)
- [12] Kahil H., Forestier M., Guitton J., in: Jenson J. Ed., *Solid State Protonic Conductors III La Grande Motte France*, Odense University Press, 84 (1984).

- [13] R. S. Daries Bella, G. Hirankumar, Prem Anand Devaraj, International Journal of Chem tech Research 6 (13) 5235-5240 (2014).
- [14] D.P.Almond, A.R.West, Solid State Ionics 23 (27), (1987)
- [15] Amor I. B., Rekik H., Kaddami H., Raihane M., Arous M., Kallel A., *Journal of electrostatics*, 67,717-722 (2009).
- [16] Daries Bella R.S., Karthickprabhu S., Maheswaran A., Ambika C., Hirankumar G., PremAnandDevaraj,*Physica B ,(Condensed Matter Physics)* , 458, 51-57 (2015).
- [17] Ross Macdonald J., (ed.) *Impedance Spectroscopy*, John Wiley and Sons, New York, Chap. 2 (1987).