

NMR studies on the composition of PVdF-HFP membrane for Li batteries

S. Radhakrishnan · M. Ganesan · N. G. Renganathan

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Abstract In the field of lithium batteries, poly(vinylidene fluoride-co-hexafluoropropylene) polymer finds extensive applications as membrane, in which the composition of polymer is very crucial for the optimum performance of the cell. In this report, nuclear magnetic resonance (NMR) study as an investigation tool has been carried out to understand the role of polymer content in the range of 10% to 30%. Also by using NMR line-width data, some clues have been drawn on the optimum polymer composition, which is in good agreement with other studies based on conductivity data.

Keywords Polymer content · Relaxation time · Correlation time · Mobility · Charge carriers

Introduction

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) electrolyte is now widely accepted for lithium (Li) batteries since it uptakes large amounts of nonaqueous liquid electrolyte and reaches liquid like conductivities at room temperature as well as exhibiting good mechanical properties [1, 2]. Essentially the morphology of the membrane plays a fundamental role in the transport of mass and ions through the porous texture. Ion transport in polymer electrolytes was studied

using nuclear magnetic resonance (NMR) [3, 4]. Ion conduction mechanism of composite gel polymer electrolyte with variation of salt and plasticizer with filler was studied using ^7Li NMR Spectroscopy [5]. Sabina abbrent et al. studied nanocomposite gel electrolyte using NMR [6]. NMR, conductivity and DSC studies of Li^+ transport in ethylene glycol/citric acid polymer gel were studied by C.E. Tambllelli et al. [7]. Conduction properties of Li gel electrolytes were investigated by impedance spectroscopy and pulse-field gradient NMR spectroscopy [8]. Ionic mobilities of PVdF-based polymer gel electrolytes were studied by direct current NMR [9]. In all these studies, investigations have been done from the technological point of view. From the physical chemistry point of view, limited knowledge exists. NMR studies have been carried out in the present investigation to understand why at 20% of polymer content the conductivity attains maximum level. Results are presented and discussed in the paper.

Experimental

PVdF-HFP (Kynar 2801, $M_w=4.77 \times 10^5$) with a copolymer ratio of PVdF/HFP=88/12 was dried in an oven under vacuum at 60 °C before usage. Ethylene carbonate and dimethyl carbonate (plasticizers) from MERCK were used as received without any treatment. In line with this, the meaning of 10% polymer content refers to the polymer (PVdF-HFP) and the rest is plasticizer (90%). In the case of 30%, a PVdF-HFP polymer content of 30% and the rest is plasticizer. The PVdF-HFP was dissolved in a mixture of acetone and tetrahydrofuran. After complete dissolution of the polymer the plasticizer was added and homogenized for about 30 min with slight heating. After some time, a homogeneous and viscous polymer solution was obtained,

S. Radhakrishnan (✉) · M. Ganesan
Central Electrochemical Research Institute (CSIR),
Karaikudi 630006 Tamil Nadu, India
e-mail: radha_1965@yahoo.com

N. G. Renganathan
Vel Tech University,
Chennai, India

which was cast over a glass plate and dried. The optimization of the plasticizer was done by trial and error method. The criteria for the optimization was to get a free-standing film when it was dried. The composition of the plasticizer was also arrived at from the literature data [10] and the present aim of this work is not to see the effect of change in plasticizer content on the PVdF-HFP membrane properties but the effect of the polymer content on the number of charge carriers and, in turn, the conductivity of the membrane.

In the case of PVdF-HFP with 1 M of LiClO_4 polymer film, the same procedure is followed. The addition of salt was made after homogenizing the plasticizer. NMR studies were carried out using the Bruker 400 MHz spectrometer.

Theory

The measurement of NMR relaxation time provides a powerful method for the investigation of atomic motion. These well-established techniques have been applied to the study of high-ionic mobility. The measurement of relaxation due to the modulation of the nuclear dipole interaction is well understood. NMR technique and complementary measurement of ionic conduction and tracer diffusion can provide a good insight into the mechanism of atomic motion in solids. Nuclei with electrical quadrupole moments are also relaxed by fluctuating electric quadrupole moments. They are also relaxed by fluctuating electric field gradients, which can arise due to the to and fro defect motion. Relaxation process is due to short range ionic motion. Quadrupolar ^7Li spin–lattice relaxation on this material yielded a minimum. This is attributed to the effect of molecular motion. Relaxation time is the decay constant for the recovery of Z component of the nuclear spin magnetization M_z towards the thermal equilibrium and these are T_1 and T_2 relaxations. They are the nuclear spin magnetization vector M . T_1 is the parallel component and T_2 is the perpendicular component. Both are relaxation and these involve redistribution of population of the nuclear spin in order to reach the thermal equilibrium distribution. A temperature difference of correlation times, determined from ^7Li NMR linewidth data analysis which is well detailed in the Bloembergen, Purcell and Pound (BPP) theory for all polymer electrolyte, was compared to two distinctive regions above and below T_{sc} . Here relaxation changes slope below and above a particular temperature. This is known as T_{sc} which is described as the temperature where the slope changes. This factor is used by us to find out the optimum composition of the polymer content to have the slope change and this gives the indication that there will be an optimum number of charge carriers which will have better conduction of Li. T_1 and T_2 are correlated

to τ_c by the expression given in Eq. 1 as given in the BPP theory.

$$[1/T_2 = C[\tau_c/(1 + \omega_0^2\tau_c^2) + 4\tau_c/(1 + 4\omega_0^2\tau_c^2)]] \quad (1)$$

Here τ_c is the correlation time [5]. If τ_c is less, then the number of charge carriers will be optimum for conduction. This is the basis for the selection of polymer content which is the criteria adopted in this paper.

Results and discussion

Figure 1 depicts the variation of relaxation time at different temperatures for the polymer PVdF-HFP containing LiClO_4 . It is seen from the figure that there is a maximum relaxation time at a particular temperature. It is also seen from the figure that the maximum occurs for 10% and 20% polymer content; whereas, the maximum will occur at a higher temperature. Between 10% and 20%, there is a shift in the maximum relaxation time and the trend is changing from a higher to a lower temperature from 20% to 10% and again the trend is changing from 20% to 30% polymer content. As indicated in the theory section, there is a change of slope in T_{sc} in between 20% polymer content and 30% polymer content and this suggests that this will be a good basis for the selection of polymer content, which will indicate the maximum number of charge carriers at 20% polymer content. This clearly indicates that there is a change in the number of charge carriers when the variation

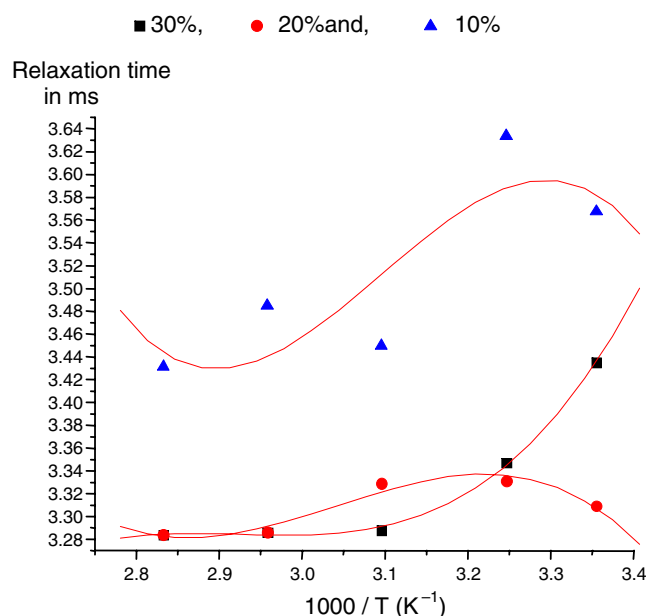


Fig. 1 Variation of relaxation time at different temperatures

of polymer content is changed from 10% to 30% and at 20% this change is predominant.

In general, line width T_2^{-1} decreases. This indicates that the mobility of ^7Li decreases. This decreases in a monotonic way. In the present case, T_2^{-1} values display a maximum at 303 K for 10% PVdF-HFP and at 313 K for 20% PVdF-HFP; whereas, for 30% PVdF-HFP, the maximum does not appear on the higher side of the temperature, but it is likely to appear at a lower temperature than room temperature where the data are not available at present. The increase detected between 303 K and 313 K may be ascribed to an increase of dipolar interactions; whereas, the shift in the maximum to the lower temperature at 30% polymer concentrations may be due to high viscosity compared to the other two polymer concentrations. The τ_c is calculated using the relation Eq. 1 [11].

From T_2 , τ_c values are obtained using a solver program in MS Excel. For various guess values of τ_c left-hand side and right-hand side values of the equation, the values are matched using a solver program in Excel. The error in this calculation is depicted in Fig. 2. The value which gives a minimum error in (matching) the two sides of Eq. 1 is noted and this is reported as τ_c . This value is given as correlation time. As per BPP theory, if the correlation time is low then the charge carrier will be optimum and this can be used as a criteria to fix the polymer content.

To see the effect of the concentration of polymer content measurement of correlation, the time for the three different polymer contents is calculated at a particular temperature (298 K) and it is tabulated in Table 1.

From this table it is clear that at 20% polymer content, the correlation time is at a minimum compared to 10% and 30% polymer content, and it is concluded that at 20% the

Table 1 Measurement of correlation time at fixed temperature (298 K)

PVdF-HFP (%)	Temperature (K)	Correlation time (s)
10	298	5.33×10^{-9}
20	298	5.048×10^{-15}
30	298	3.36×10^{-13}

number of charge carriers are considerable and the conductivity is at a maximum at room temperature.

Figures 3 and 4 also show the effect of the polymer on the mobility of the charge carrier in the more microscopic range from the spin–lattice relaxation time variation with temperature. Assuming that the temperature dependence of T_1 of the solution without polymer showing a symmetrical behavior (as indicated in Fig. 1) increase in polymer content, the plot appeared to be asymmetric in form and exhibits a maximum at higher temperature and minimum at lower temperature. This asymmetry is due to a new relaxation process by gelation. The component of the low-temperature (room temperature) region is almost consistent with the relaxation process of the solution and here too at 20% PVdF-HFP the relaxation time is lowest compared to 10% and 30%; whereas, at a higher temperature from the extended symmetry behavior, it can be seen that the polymer content affects the mobility of charge carriers through the relaxation process of high-temperature component. The deviation of the temperature dependence plot of T_1 from the symmetry curve of the solution may be due to the amorphous nature in the gel and this has happened because of the interaction between the polymer and the electrolyte [12]. The effect of the polymer on the mobility

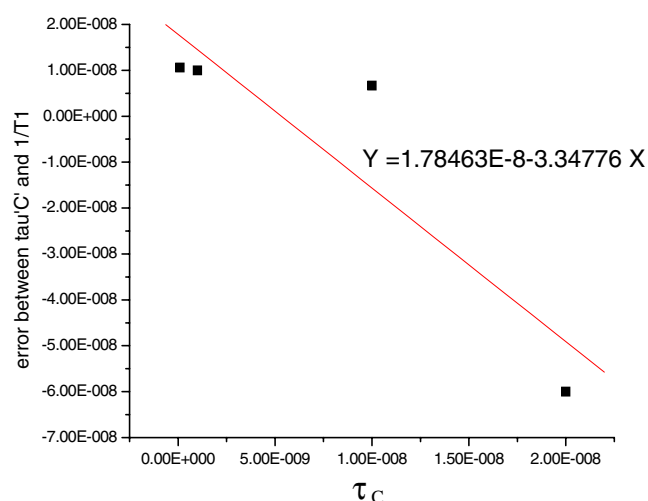


Fig. 2 Error obtained in the calculation of τ_c and $1/T_1$ vs τ_c in the equation cited in the text

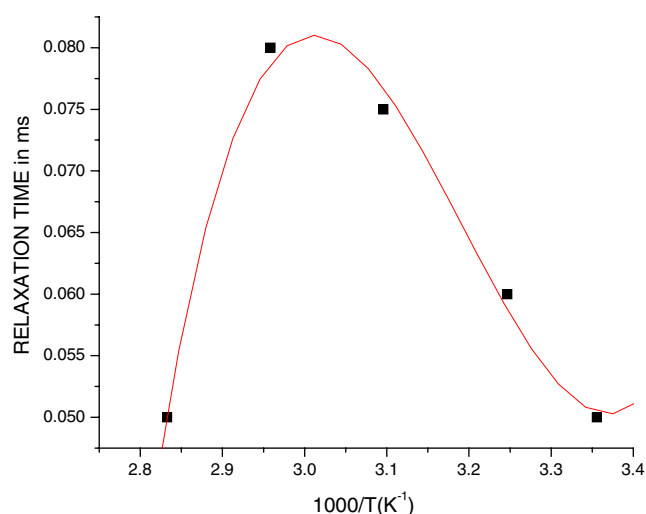


Fig. 3 Relaxation time vs temperature of 10% polymer

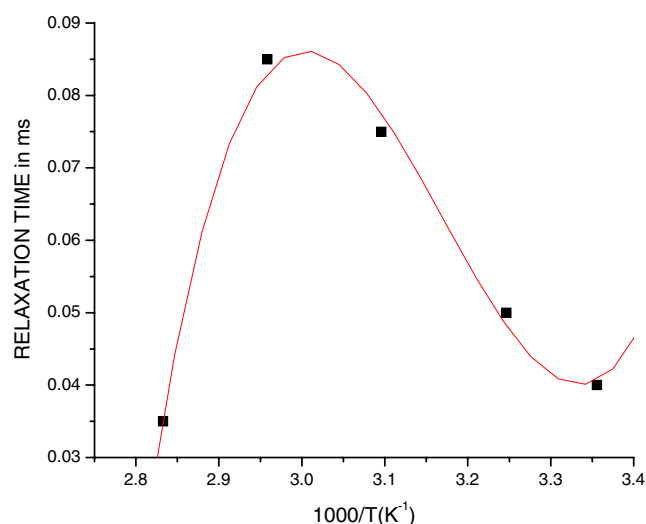
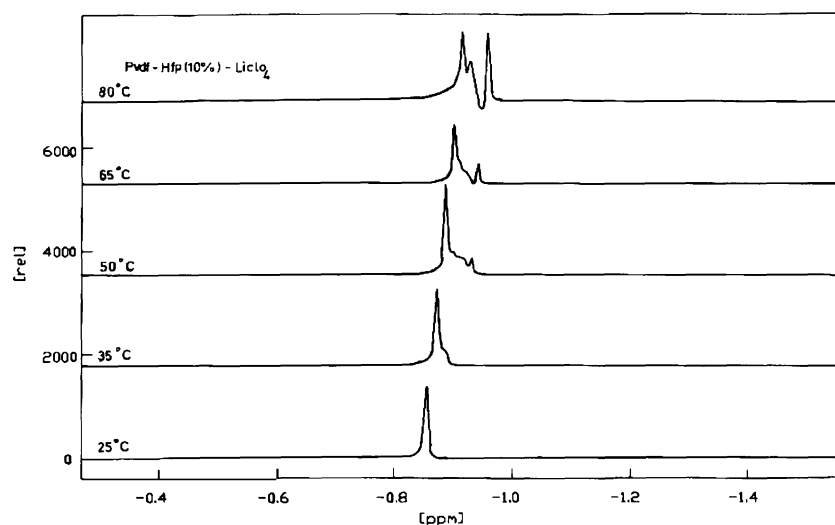


Fig. 4 Relaxation time vs temperature of 20% polymer

of the charge carrier may be due to the effect of degree of dissociation of the salt, and hence, the chemical interaction effect of the polymer is the major contribution to the mobility of the carriers in this type of gel electrolytes.

For the ^7Li cations, over the entire measured range, the time scales is in the diffusive hopping and not corresponding to segmental motion. The time constant follows one kind of thermally activated behavior at a temperature of 330 K and another one at a temperature above 340 K as is evident from Figs. 3 and 4. At intermediate temperature the data exhibit some curvature. This suggests, as already discussed, that there is a change in the slope in the curve of relaxation time versus temperature. This fact is of use in deciding the number of charge carriers. This fact also suggests that the correlation time does not change with the other temperatures for the given composition.

Fig. 5 NMR spectra for PVdF-HFP (LiClO_4 , 10%) electrolyte

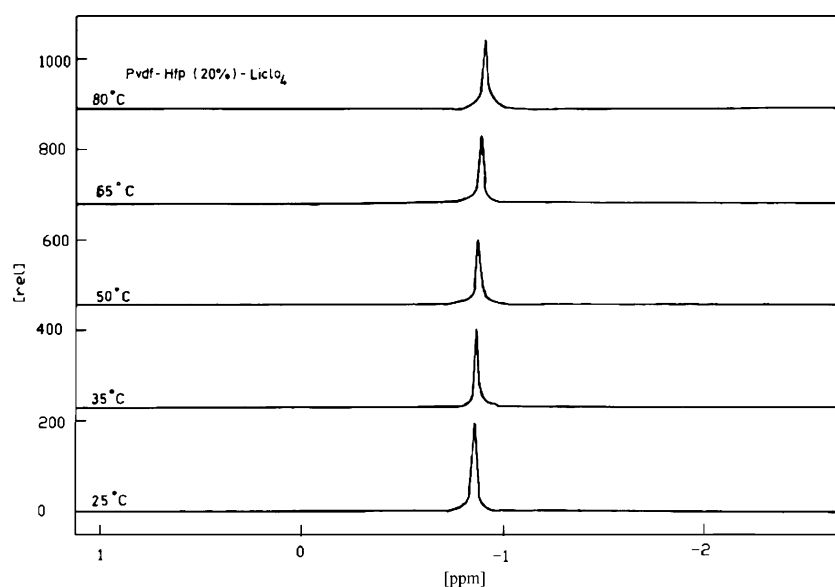


Information about the molecular motions can be extracted from variable temperature data. Similar to Eq. 1, another equation can be thought of to describe homonuclear spin–lattice relaxation by the dipole–dipole interaction. Figures 3 and 4 are typical graphs showing the relaxation time variation with temperature for 10% PVdF-HFP with Li perchlorate as salt at 90 ppm from CF_2 by ^{19}F nuclei. Similarly, for the other two compositions, 20% and 30% PVdF-HFP, the minima are taken from these graphs. Figure 4 is provided to indicate the minimum obtained for 20% PVdF-HFP, which is well exhibited; whereas, for the 30% PVdF-HFP (for which a figure is not provided) it is not so and probably it could have been obtained at a lower temperature where the data are not available.

Like the above for the ^{19}F nuclei, two regions namely, 75 ppm and 90 ppm, and for ^1H nuclei, two regions at 1 ppm and 3 ppm, the relaxation time versus temperature graph were made and correlation time versus temperature have been calculated. These data are very much similar to the one that has already been discussed and no further discussion was attempted.

As already indicated, at 20% PVdF-HFP, the Li ions are more mobile at room temperature compared to other compositions. This is also evident from the NMR shift, which is shown in Figs. 5, 6 and 7. It is seen from Figs. 5, 6 and 7 that there is a clear variation in the electronic conduction mechanism when polymer content is steadily increased and as already obtained from the correlation time data it is concluded that 20% polymer content is optimum for better conductivity. At 10%, enough charge carriers are not available for conduction. At 30%, more charge carriers are available but due to association, the conductivity has come down. At 20%, sufficient charge carriers are available for optimum conduction. It is seen from the figures that there is a change in peak width. At 10%, polymer content

Fig. 6 NMR spectra for PVdF-HFP (LiClO_4 , 20%) electrolyte

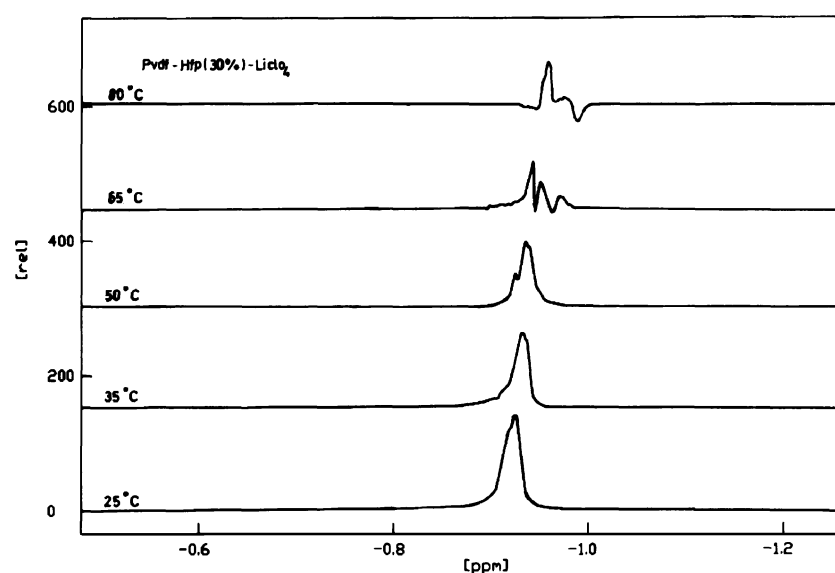


peak is not only sharp but split. At 20%, polymer content peak width is uniform and not distorted. At 30%, the polymer content peak is broad but it is also split and distorted.

Conclusion

1. PVdF-HFP electrolyte with 1 M LiClO_4 electrolyte composition with polymer content 20% is found to be the best from the NMR studies, which goes well with good conductivity data.
2. A $1/T_2$ decrease is associated with the decreasing mobility of Li and for 20% PVdF-HFP, maximum occurs at 313 K.
3. The correlation time is lowest for PVdF-HFP for 20% polymer content compared to the other two polymer contents viz 10% and 30%, and this indicates the mobility of charge carriers, which is high in 20% compared to 10% and 30%.
4. From the NMR spectra, the possibility of the composition, where charge carriers will be at maximum, is indicated in this communication. At 20% polymer content there is no distortion of the spectra.

Fig. 7 NMR spectra for PVdF-HFP (LiClO_4 , 30%) electrolyte



References

1. Manuel Stephen A, Gopu Kumar S, Renganathan NG, Anbu kulandainathan M (2005) *Eur Polym J* 34:6955–6955
2. Manuel Stephen A, Gopu Kumar S, Renganathan NG, Dale-Teeters (2004) *Mater Chem Phys* 85: 6
3. Saita Y, Kataoka H, Stephen AM (2001) *Macromolecules* 34:6955
4. Adebahr J, Best AS, Byrne N, Jacobson P, Macfarlane DR, and Forsyth M (2003) *Phys Chem Chem Phys* 720–725
5. Saikia D, Chem-yang YW, Chem YT, Li YK, Lin SI (2009) *Electrochimica Acta* 1218–1227
6. Sabima Muthu, Emmanul, Giannolis P (2003) *Electrochimica Acta* 2113–2121
7. Tambelli CE, Donoso JP, Magon CJ (2007) *Electrochimica Acta* 1535–1540
8. Yuria Saito, Hiroaki Kataoka, Tetsu Sakai, Shigehito Peki, (2001) *Electrochimica Acta* 1747–1751
9. Hiroshi Kataoka, Yuria Saito, Yoshinori Miyazaki, Shigehito Deki (2002) *Solid State Ionics* 175–179
10. Roux C, Gorecki W, Sanchez JY, Belorizky E (1998) *Electrochim Acta* 43:10
11. Vladimir IB (Ed) *Practical NMR relaxation for chemists* (2004) John Wiley & Sons Ltd, England, Chapters 7 and 11
12. Verhoeven VWJ, De Schepper IM, Nachtegaal G, Kentgnes AKelder EM, Schoonmam J, Mulder FM (2001) *Phys Rev Lett* 86:1