



Electrical Properties of Plasticised Proton Conducting MG49 Polymer Electrolyte

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ABSTRACT

A free-standing film consisting of 49% PMMA grafted-natural rubber electrolytes was prepared. Potassium hydroxide (KOH) and propylene carbonate (PC) was added to the preparation and the properties of the electrolytes measured using complex impedance analysis at various temperatures. The addition of plasticiser in alkaline polymer electrolyte gives rise to the ionic conductivity up to $2.647 \times 10^{-6} \text{ S cm}^{-1}$ at composition consisting of 50wt.% of PC. The dielectric properties of the GPEs were studied and the relaxations at higher frequencies appear in both imaginary and real part of the permittivity. These relaxations are related with the interface ion polarisations at the polymer-electrode interface and segmental motion of the polymer electrolyte molecular chains. The influence of the impedance spectra on temperature was studied. Results showed rising temperature increased conductivity, top frequency (f^*), relative dielectric constant (ϵ_r) and geometrical capacitance (C_g) due to the mobility of free ion carriers

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INTRODUCTION

Proton-conducting electrolytes have been identified as promising separator in batteries, supercapacitors and fuel cells (Qiao et al., 2010, Zukowska et al., 2000). Alkali-based

electrolytes exhibit high proton conductivity even at temperatures below 370 K (Zukowska et al., 2000; Nikulin et al., 2014). Metal hydroxides containing hydrogen have been attracting attention as promising proton conducting materials with unique characteristic of occupying an intermediate position between electronic and ionic conductors (Qiao et al., 2010). Potassium hydroxide (KOH), the subject of investigation in this paper, is an alkali metal that provides hydrogen or proton charge carriers in the electrolytes (Nikulin et al., 2014). However, safety issues concerning the commercial batteries using alkaline liquid based electrolytes make them unsuitable for practical use. Thus, an alternative is solid polymer electrolytes as the problems resulting from usage of liquid electrolytes can be avoided to a great extent. Polymer electrolytes are known for their good mechanical properties and ease of fabrication (Mohamad et al., 2008; Chandra et al., 2002). Unfortunately, these solid polymer electrolytes suffer low conductivity at room temperature. Hence, to improve conductivity, several techniques are useful, such as grafting, plasticisation (Woo et al., 2013; Zaki et al., 2012), polymer blending (Alias et al., 2012) and fillers (Adam et al., 2012). Plasticisation involves adding a substantial amount of plasticiser into the polymer matrix which produces gel polymer electrolytes (GPEs) (Kato et al., 2002). Plasticisers have been proven to soften the rigid polymer chain, allow greater mobility of charge carriers, and lower the glass transition temperature (Chandra et al., 2002; Alias et al., 2005; Kamisan et al., 2010). Plasticisers of low molecular weight and high dielectric constant are frequently selected, such as propylene carbonate (PC), ethylene carbonate (EC), dimethylformamide (DMF), etc (Latham et al., 2002). These plasticisers were reported to be compatible with poly (methyl methacrylate) (PMMA) and accommodate the enhancement of conductivity (Alias et al., 2005). The MG49 is a polymer consisting of natural rubber grafted with 49% PMMA and the former is suitable to be applied as polymer host of electrolytes. The MG49 contains functional groups of carbonyl (C=O) and carboxyl (C-O-O-H), which will covalently bond with the hydroxide ions (OH⁻) of KOH. The high permittivity and high dielectric constant of MG49 assist in ionization of salt providing high concentration of charge carriers.

This paper studies the properties of plasticised alkaline based polymer electrolyte using MG49 as the polymer host and KOH as the proton charge contributor. The existence of lone pairs in the molecular structure of the polymer host makes it possible for the complexation of salt-polymer, whereas the cation will be attracted to the lone pairs and enhancing the ion diffusion inside the polymer matrix simultaneously produces free ions (Mahmud et al., 2012). The diffusion and mobility of free ions contribute to ionic conduction while the electrolytes were introduced with propylene carbonate (PC) as the solvent (plasticiser). The electrical properties of MG49-KOH-PC polymer electrolytes are presented and discussed.

METHOD

Sample Preparation and Characterisation

The GPE films comprising MG49-KOH-PC were prepared by solution casting technique. MG49 (Rubber Research Institute of Malaysia, RRIM), potassium hydroxide (KOH) (Aldrich) and propylene carbonate (PC) (purity 98%, Aldrich) were used. The KOH salt was vacuum dried for 12 hours at 383 K prior used. 1.0 g of MG49 was dissolved in 25 ml tetrahydrofuran

(THF) (Aldrich, $\geq 99.9\%$) and was doped with potassium hydroxide (KOH). The solution was then stirred continuously with magnetic stirrer for several hours at room temperature. The homogeneous solution was then cast onto petri dish and allowed to naturally dry in the fume hood at room temperature. The remaining solvent in the cast solution was removed by drying it in vacuum oven for 48 hours at 333 K. Various stoichiometric ratios of KOH and MG49 were then repeated as above procedure. The sample with highest ionic conductivity was selected and added with different weight percent of PC to prepare GPEs in a similar way. The obtained films were stored in desiccator for further use.

The prepared films were studied through impedance data taken from the impedance spectroscopy. The electrolyte films were first sandwiched between two stainless steel blocking electrodes with cross-sectional area of 0.196 cm^2 and connected to HIOKI 3532-50 HiTester Impedance Spectroscopy. The impedance spectroscopy was logged over a frequency range of 1-106 Hz. The samples were placed in a humidity chamber for controlled temperature between 30°C to 100°C .

RESULTS AND DISCUSSION

Nyquist plot studies

Nyquists were plotted to study the ion interaction in the polymer electrolytes. Figure 1(a) and Figure 1(b) shows the Nyquist plot of cells assembled by MG49-KOH-PC electrolyte with stainless steel electrode at 303K. During the impedance test, the polymer electrolytes were placed in between two stainless-steels (SS). The SS acts as a blocking electrode for ion transportation, and an inert electrode for the polymer electrolyte. As a result, a linear line was observed at 10 and 20 wt.% of PC as in Figure 1(a). The plot however was transformed into an inclined arc at higher content of PC. The inclined arc is often observed in Nyquist plane for rough electrodes where a Faradaic reaction takes place in addition to capacitive charging (Bosco et al., 2008).

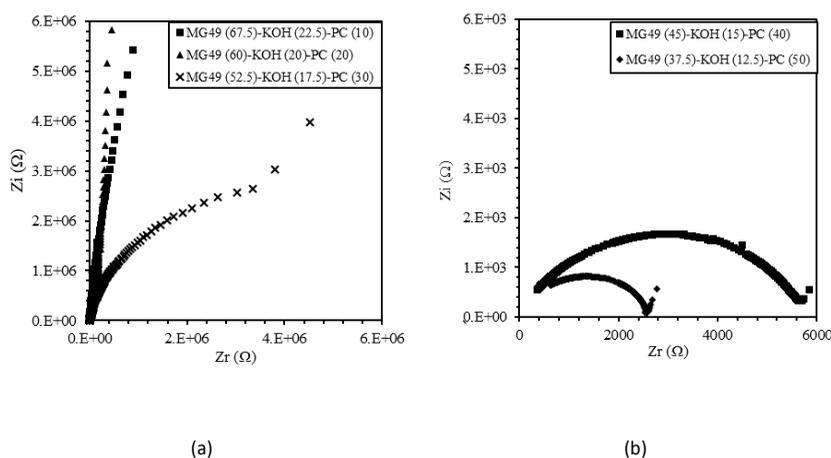


Figure 1. (a), (b) Nyquist plot for MG49-KOH samples of various wt. % PC

The addition of 40 and 50 wt.% of PC results in one semicircle at high frequency range as in Figure 1(b). The intersection of the semicircle and the straight line reflects the bulk resistance R_b of the polymer electrolyte. The straight line in low frequencies is attributed to the ion diffusion in the electrolyte (Xu et al., 1998). The ionic conductivities were calculated based on the following equation:

$$\sigma = \frac{t}{(A.R_b)} \quad [1]$$

Where (R_b) is the bulk resistance, A and t are the electrolyte film surface area and thickness respectively. The ionic conductivities for each sample are shown in Table 1. At higher wt.% of PC, the Nyquist plot is compressed to smaller inclined arc (as in Figure 1(b)), whereas the bulk resistance decreases to smaller values. This indicates that the addition of more plasticiser improves the electrode-electrolyte contact. Plasticiser helps improve the flexibility of the electrolyte, hence increasing its contact with the electrode. The bulk resistances of the samples were also reduced. The good electrode-electrolyte contact contributes to more surface contact area for the ion polarisation to induce and simultaneously increase the conductivity of the polymer electrolyte. The ion polarisation is further investigated through the dielectric relaxation of each sample. The presence of plasticiser also favours the ionic mobility that correlates with the flexibility of the polymer host due to the creation of free volume (Adam et al., 2012; Hashim et al., 2010).

Table 1
Bulk Resistance (R_b) and conductivity values (σ) for MG49-KOH containing different wt. % of PC

PC content (wt. %)	Bulk Resistance, R_b (Ω)	Conductivity, σ (S.cm ⁻¹)
10	5.34x10 ⁷	2.408x10 ⁻¹⁰
20	3.25x10 ⁸	4.210x10 ⁻¹¹
30	9.52x10 ⁶	1.348x10 ⁻⁹
40	8.01x10 ³	1.331x10 ⁻⁶
50	3.23x10 ³	2.647x10 ⁻⁶

Dielectric relaxation studies

Dielectric relaxation is studied to investigate the ion polarisation for samples of different wt.% of PC. The distributions of dielectric constants with frequency are shown in Figure 2. Both real and imaginary parts of dielectric constant rise abruptly at low frequencies (approximately < 3000 Hz) confirming a strong polarisation effect on the blocking electrodes. The ion polarisations are induced by the current flowed through the system. The dipoles within the polymer electrolyte tend to rotate and align according to the electric field applied, resulting in diffusion of ions which accumulate at the electrode-electrolyte interface (Mahmud et al., 2012). The accumulation of ions results in polarisation effect, thus, producing high dielectric values (Sotta et al., 2010; Sheha et al., 2012). These dielectric constant values were observed to be larger at higher content of PC from 10 wt.% to 50 wt.%. The presence of low molecular

weight PC causes the polymer electrolyte to be more flexible, contributes to the increase of ion polarisation occurrence at the electrode-electrolyte interface due to higher surface contact, as proven by the Nyquist plot study. The flexibility is also due to the amorphous nature of the MG49 polymer electrolyte (Mahmud et al., 2012).

At high frequencies though, both real and imaginary dielectric constants were observed to decrease. In this stage, the dipoles are unable to follow the field variation at high frequencies as the periodic reversal is too fast for the dipole to orientate according to the field orientation, causing the dipole to appear ‘frozen’ (Saroj et al., 2013).

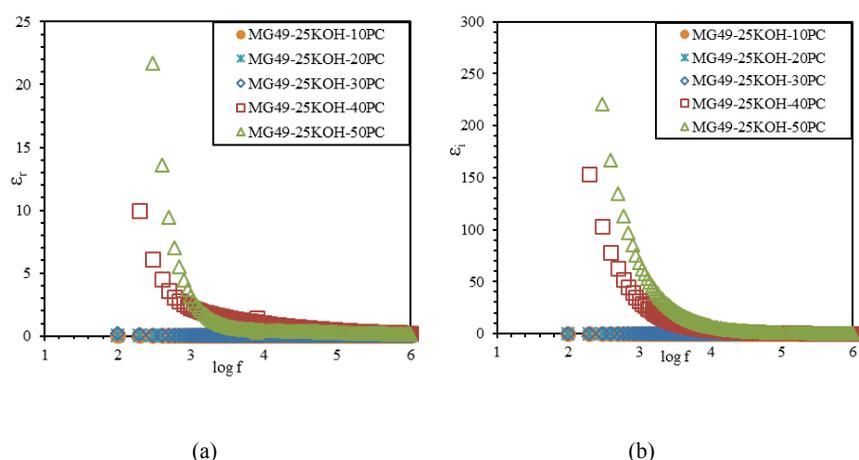


Figure 2. (a) Real; and (b) imaginary part of dielectric constant versus frequencies for MG49 – 25 wt.% KOH with different wt.% of PC

Impedance analysis for varying temperatures

The electrical properties of MG49-KOH-PC samples at different temperatures were studied. The total impedance of the stainless steel (SS) electrode, C_r and Z_w represent the bulk resistance, the real part of the electrolyte capacitance and the Warburg impedance. The real part of the polymer electrolyte capacitance can be expressed as,

$$C_r = A\epsilon_0\epsilon_r/l \quad [2]$$

where ϵ_0 (equal to $8.85 \times 10^{-14} \text{ F cm}^{-1}$) is the dielectric constant of vacuum, ϵ_r is the real part of the dielectric constant of the studied electrolyte film, A is the electrolyte film surface area (cm^2) and l is the electrolyte film thickness (cm). The top frequency, f^* of the impedance spectrum can be expressed as a function of ionic conductivity, σ as below,

$$f^* = \sigma/(2\pi\epsilon_0\epsilon_r) \quad [3]$$

Utilising these equations, the relative dielectric constant (ϵ_r), ionic conductivity (σ), the top frequency (f^*) and the real part capacitance (C_r) of MG49-KOH-PC film can be determined according to the impedance spectrum.

The ionic conductivity, top frequency, relative dielectric constant and geometrical capacitance at various temperatures for MG49-KOH-PC film were plotted as shown in Figure 3(a), (b), (c) and (d). These four parameters appeared to increase with increasing temperature. This is due to the mobility of free ion carriers facilitated by the increment of the segmental motion of the polymer molecular (Woo et al., 2013; Xu et al., 1998; Mahmud et al., 2012). The increase in temperature significantly increases the amorphous nature of the polymer electrolytes, thus providing bigger free volume in the system and increasing the conductivity. Consequently, the increase of temperature will increase the internal energy to the polymer chain allowing it to push against its neighbouring atoms, thus creating more free volume.

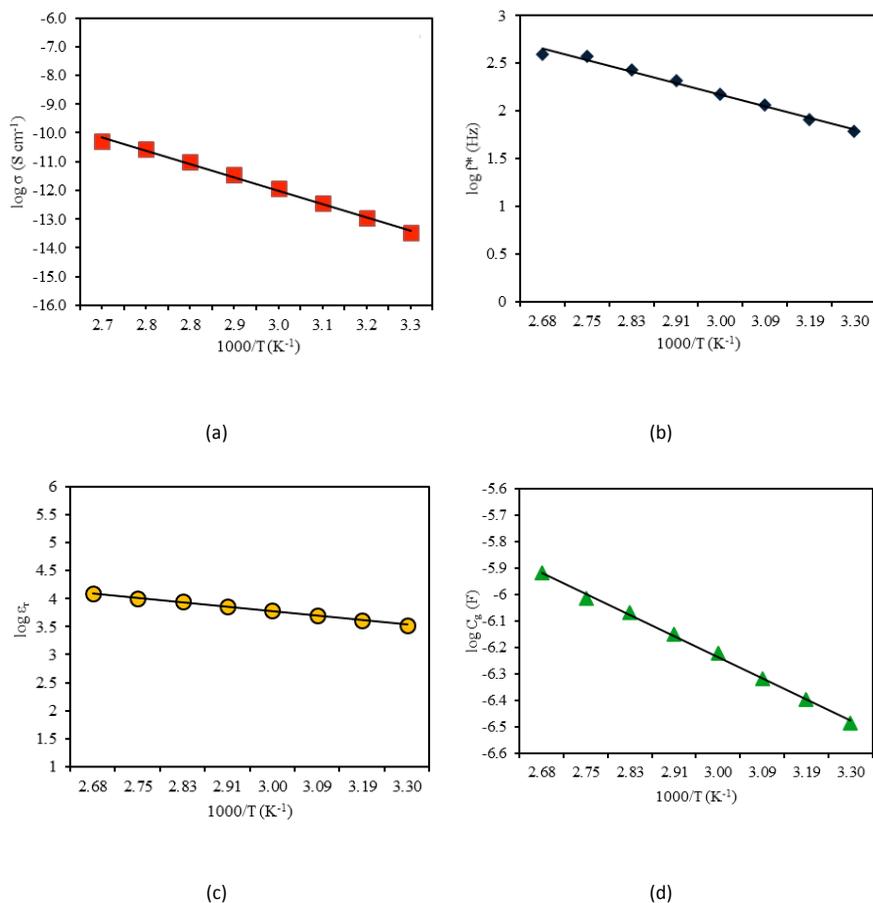


Figure 3. The influence of temperature on the: (a) ionic conductivity (σ); (b) top frequency (f^*); (c) relative dielectric constant (ϵ_r); and (d) geometrical capacitance (C_g) of MG49-25KOH-50PC

CONCLUSION

This study had focused on the role of plasticiser in alkaline based polymer electrolytes in term of its impedance properties. The addition of plasticiser, PC, inside the polymer matrix were observed to increase the ionic conductivity up to $2.65 \times 10^{-6} \text{ S cm}^{-1}$, achieved by MG49-KOH sample containing 50 wt.% PC content. The PC consequently improved the polymer electrolyte flexibility, and provided better electrode-electrolyte contact, whereas its low molecular weight properties provided larger free volume inside the polymer system. The dielectric relaxation indicated improved electrode- electrolyte contact whereas more surface contact area for ions polarisation.

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