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RESEARCH ARTICLE

Increasing the ionic conductivity of solid state polymer electrolyte using fly ash as a filler

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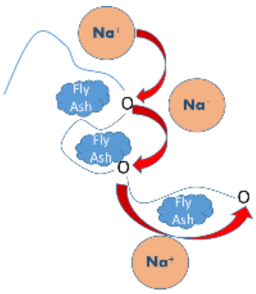
Graphical abstract



Abstract

Polymer electrolytes film based on polyethylene oxide (PEO) complexes with $NaClO_4$ salt with a ratio of EO: Na = 20:1 and fly ash as filler has been prepared by solution casting technique. The crystallinity of the solid polymer electrolyte was characterized by X-Ray Diffraction (XRD). The interaction between PEO and Na-ions confirmed by Fourier Transform Infra Red (FTIR) analysis. The ionic conductivity of the solid polymer electrolyte was investigated by impedance analysis from 1 MHz to 1 Hz at a varied temperature of 50°C, 60°C, 70°C, 80°C, and 90°C. The maximum ionic conductivity of EO: Na = 20 was 5.31×10^{-5} S cm^{-1} and increases to 2.13×10^{-4} S cm^{-1} by the addition of fly ash 5% at the temperature of 60°C.

Keywords: Polymer electrolyte, PEO, conductivity, $NaClO_4$, fly ash

INTRODUCTION

A battery is essentially a device that store chemical energy converted into electrical energy. Basically, the battery is a small chemical reactor with a reaction to produce energetic electron that ready to flow through the electrical device. The use of a battery as an energy storage device is very wide, for example, mobile phone, children toys, electrical watch, laptop, electric vehicles, etc. The first battery was invented by Allesandro Volta in 1800. He stacked the disc of Cu and Zinc that separated by a cloth soaked in salt water. Wires connected to either end of the stack produced a continuous stable current. Each cell (a set of Cu, Zn disc and the brine) produces 0.76 V of electricity.

The advancement of twenty-first century civilization, making the demand for a portable battery and stationary energy device increasing. Currently, rechargeable battery technology is based on Li-Ion technology. Lithium batteries have been widely applied in the automotive industry, portable devices, and applications on the aerospace devices, which have been the subject of concern at the moment, both drawing attention to battery developers/researchers as well as producers (Dias et al., 2000).

The lithium battery has a lower self-discharge rate, therefore, has a longer shelf life and has a high energy density, hence reliable as energy storage (Ni'mah et al., 2015). There are 2 types of lithium batteries in the application, bulk batteries and micro batteries. The micro-battery is still under development. The rapid development of information technology and electronics towards the direction of multifunction, high integration and the need for high electrical energy resources to move electronic devices into miniaturization. Lithium microbonomics is an ideal energy storage device for biological/medical equipment (pacemakers, hearing aids, defibrillators, etc.) (Wang et al., 2015).

We must remember with the many applications of lithium batteries that lithium metal sources may not be able to meet the amount of market demand. Researchers are trying to find alternative materials to overcome the scarcity of lithium. The perfect candidate to replace lithium appears to be sodium, because sodium has an abundance in nature more than lithium (Li: Na = 1: 1000 backup ratio), a relatively low cost of sodium that is 150 \$ ton^{-1} whereas for Lithium it costs 5000 \$ ton^{-1} (Kuze et al., 2013) and the redox potential is very suitable (Eo $Na^+/Na = -2.71$ V vs. SHE, only 0.3 V above that of Lithium) (H. Pan, 2013). A number of research and battery development efforts are underway to develop Na^+ ions as electrolytes and compatible electrode materials for NIB (Vignarooban et al., 2016). In addition, sodium is the "top six" of the most abundant elements in the earth's crust, which makes it much cheaper than lithium.

Sodium batteries were first discovered in 1870 in the form of Na (Hg)-C cells, but the Sodium batteries were not applied commercially due to low energy density. This limitation impedes progress in research on Sodium batteries for over 100 years. After this long stagnation period, the next generation of Na batteries, in 1960 (Na-S), and 1980 ($NaNiCl_2$) both of which still showed low energy density (Bitner-Michalska et al., 2016).

Batteries are composed of three main components, namely cathode (negative electrode), anode (positive electrode) and electrolyte. The cathode on the Sodium-ion battery is Na_2MnSiO_4 (Law et al., 2017), and the cathode may be a carbon bar. Sodium-ion battery anodes for example Nb-doped TiO_2 ($Ti_{0,94}NB_{0,06}O_2$) (Usui et al., 2016). The electrolyte is NaFSA (sodium bisphluorosulfonylamide) 0.25 M dissolved in N-methyl-N-propylpyridinium-bis-fluorosulfonylamide (MPPFSA) (Dahbi et al., 2017).

Liquid electrolytes have several disadvantages such as leakage and gas formation during solvent decomposition (Ye, 2012). One of the alternative to solve the problem is by developing solid electrolyte, or called Solid Polymer Electrolyte (SPE). SPE may overcome some of the problems attached to liquid electrolyte batteries, less harmful than liquid electrolytes, electrode systems have a non-flammable electrolyte, better storage capacity and in term of safety, it will not leak as in liquid electrolyte. All kinds of SPE is one type of new battery with an excellent level of security and energy density. The replacement of liquid electrolyte batteries with SPE enables simplification of cell structures, and more compatible dimensions (Kim et al., 2015).

SPE consist of polymers as the matrix or main ingredients, in which electron migrate and inorganic salts such as Li, Na, and Mg have been developed by many scientists to extend the function and application of SPE. Polyethylene Oxide (PEO) has been used as a SPEs matrix because of its low glass transition temperature (Tg, 213 K) and its ability to dissolve inorganic salts. The PEO-specific electrolyte conductivity is 10^{-7} S cm^{-1} at room temperature. This value is about 4-5 times lower than the ionic conductivity of liquid electrolyte/Ionic Liquids (10^{-3} S cm^{-1}). Many scientists have investigated a new type system to improve the conductivity or performance of SPE. The four basic approaches to improve the conductivity or performance of SPEs are (1) lowering Tg of SPE, (2) preventing crystallization of SPE matrix, (3) increasing inorganic salts solubility in SPE, and (4) adding anion groups to SPE matrices which able to increase the number of cation transfers (Dahbi et al., 2017).

Although the four approaches have been implemented, SPE still has limitations due to its low conductivity. An effort to raise the conductivity of polymers electrolyte is by fillers addition during the preparation of polymer electrolyte films, for example, the addition of Al_2O_3 (Yap et al., 2015), TiO_2 (Ni'mah et al., 2015), SiO_2 (Ketabi and Lian, 2013), etc.

PEO containing alkali metal ions still exhibit relatively low ionic conductivity compared to liquid/aqueous electrolytes. In general, the PEO-based composite electrolyte is a mixture of crystalline and amorphous phases with the ratio of which depends to a great extent on compositions of the electrolyte, temperature, and thermal stability (Singh et al., 2015).

From several previous studies, it has been applied some metal oxide is used as a filler which can increase the ionic conductivity of Solid Polymer Electrolyte. Nowadays a lot of research has been done about Fly Ash which contains many metal oxides such as SiO_2, Al_2O_3, etc. Fly ash (FA), a waste by-product is generated abundantly by combustion of coal in thermal power stations. It is a mixture of oxides rich in silicon (SiO_2), iron (Fe_2O_3), and aluminum (Al_2O_3) (Kumar et al., 2012).

Fly Ash composition rich in metal oxide and also fly ash is a waste by-product from coal combustion so it's cheap and easy to obtain. So in this study, it is expected that fly ash filler can increase the conductivity of Solid polymer electrolyte.

EXPERIMENTAL

Materials

Poly ethylene oxide (PEO) with a molecular weight of 600.000 Sigma-Aldrich, sodium perchlorate 99% ($NaClO_4$), acetonitrile, fly ash from Paiton Electric Steam Power Plant, East Java, Indonesia was used to prepare polymer electrolyte.

Synthesis of solid polymer electrolyte with filler

The required amount of PEO, $NaClO_4$ (EO: Na = 20) and fly ash with different concentration (0%, 1%, 3%, 5% and 7%wt) were added to 5 mL acetonitrile and stirred until a homogenous mixture was obtained. The mixture then poured into a Teflon petri dish with 2 cm diameter and the solvent evaporated in an oven at 55˚C for 6 h. The final electrolyte film was 2 cm in diameter and 0.2 mm in thickness.

RESULTS AND DISCUSSION

PEO/$NaClO_4$/Fly Ash synthesis was carried out by adapting the PEO/$NaClO_4$/TiO_2 synthesis procedures (Ni'mah, 2015) as well as the preparation of Al_2O_3 concentration (Yap, 2015) and SiO_2 (Ketabi, 2015) fillers were replaced by fly ash. The appearance of the synthesized polymer electrolyte film is shown in Figure. 1. The synthesis result was a pure PEO polymer that was clear and hard. Synthesized PEO-$NaClO_4$ with 1:20 ratio produce a clear white turbid color and milder. PEO: Na + Fly Ash 5% has a soft structure and the color was yellow-brown due to the influence of Fly Ash filler.

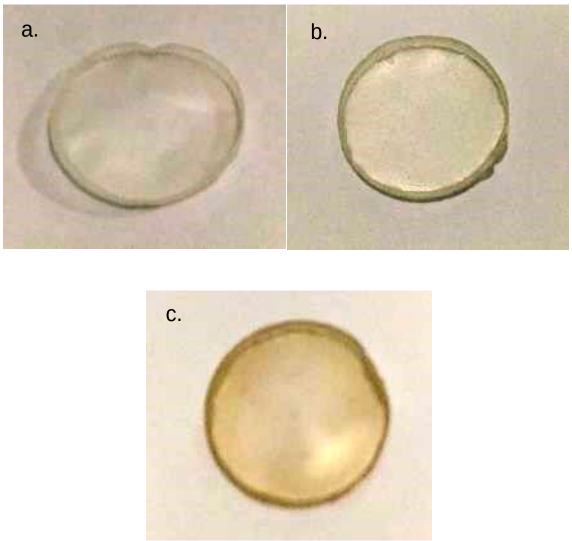


Figure 1. The synthesis product a. Pure PEO, b. Solid Polymer Electrolyte (PEO:Na = 20), c. PEO: Na + Fly Ash 5%.

The composition of fly ash from Paiton Electric Steam Power Plant was presented in Table 1. The major components of fly ash were Si, Al and Fe. The other elements such as Ti, P, S, Mg, Cl, K, Ca, Fe, Zn and Sr, occur as minor constituents in the samples. Fly Ash composition such as Al_2O_3, SiO_2, Fe_2O_3, and TiO_2 have been studied as solid polymer electrolyte filler. Thus, fly ash from Paiton Electric Steam Power Plant suitable to be used as Solid Polymer Electrolyte filler.

Table 1. The composition of fly ash collected from Paiton Electric Steam Power Plant.

Compound	Concentration %
Al_2O_3	23
SiO_2	44
SO_3	1.1
K_2O	0.999
CaO	16.3
TiO_2	0.723
V_2O_5	0.02
Cr_2O_3	0.01
MnO	0.15
Fe_2O_3	13
NiO	0.008
CuO	0.025
ZnO	0.026
Rb_2O	0.01
SrO	0.059
ZrO_2	0.022
BaO	0.23
HgO	0.02

Figure 2 shows the XRD pattern of the solid polymer film. Two peaks were observed, the first peak of 0% fly ash film was at $2\theta = 19.41$ and 1% fly ash film at $2\theta = 19.29$. The second peak of 0% fly ash film was at $2\theta = 23.75$ and 1% fly ash film at $2\theta = 23.57$.The peaks of PEO: Na Fly Ash 0% and PEO: Na Fly Ash 1% were higher than the other. The peaks of PEO: Na Fly Ash 3% and PEO: Na Fly Ash 5% were lower than PEO: Na, PEO: Na+FlyAsh 1%. On the other hand PEO: Na Fly Ash 7% the peak was the lowest.

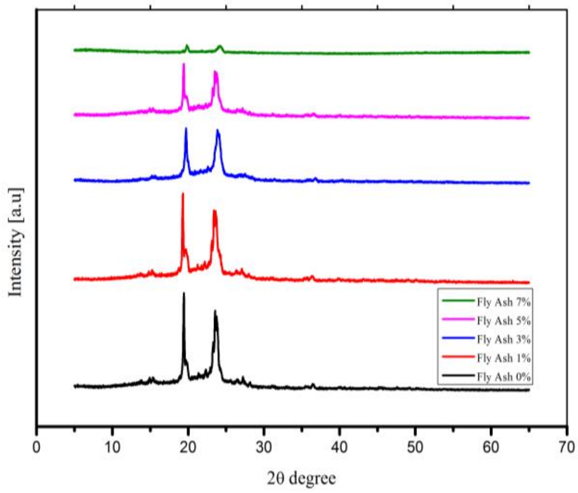


Figure 2. Black pattern = PEO:Na, red pattern = PEO:Na+FlyAsh 1%, green pattern = PEO:Na+FlyAsh 3%, blue pattern = PEO:Na+FlyAsh 5%, cyan pattern = PEO:Na+FlyAsh 7%.

Figure 3 shows the XRD pattern of pure PEO that has 2 strong peaks at 2θ = 19.2 and 23.6°. The diffractogram confirms the present of PEO-hosted polymer blend system that possesses both crystalline and amorphous regions. In contrast, the addition of NaClO$_4$ to the host polymer blend (PEO) decreases the peak intensity, suggesting a decrease in the degree of crystallinity of the PEO backbone. The XRD pattern shows that PEO: Na film without fly ash has both crystalline and amorphous phase but not for that with fly ash 5%. The diffractogram shows that as fly ash content increase the crystalline phase decrease. This indicated that the addition of fly ash to solid polymer electrolyte decrease the crystallinity of the polymer. No sharp peaks were observed for polymer film with high fly ash concentration.

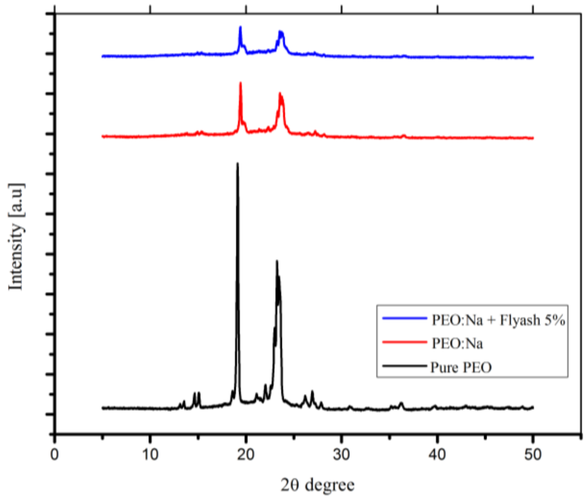


Figure 3. Black pattern = Pure PEO, Red pattern = PEO:Na, Blue pattern = PEO:Na + Fly Ash 5%.

The decrease of crystallinity makes the properties solid polymer electrolyte change. Amorphous polymer electrolyte matrix facilitates the transfer of Na$^+$ in the matrix, with the increase of Na$^+$ ion mobility in the matrix the transfer of charge increases so that the Solid Polymer Electrolit becomes more conductive (Chandra et al., 2012) (Sreekanth, 2014).

Figure 4 shows the DSC thermograms for PEO: Na and PEO: Na films with different weight percentages of fly ash. The variations of melting temperature (Tm) of endothermic peak, were measured as a function of fly ash concentration. Melting temperature of PEO: Na was ~ 67°C. The addition of 1%, 3%, 5% and 7% fly ash caused the melting temperature decrease to ~ 65°C, ~ 64°C, ~ 62°C, and ~ 60°C, respectively. Thus, from the DSC of solid polymer electrolyte with different fly ash content, it is concluded that by increasing fly ash content, the melting temperature was decreased. The melting point also correlated to the electrical conductivity. At around the melting point, the electrical conductivity of the film increase. It can be seen in Figure 5 that the maximum conductivity was at a temperature of 60°C when 5% fly ash added (Thakur et al., 1999).

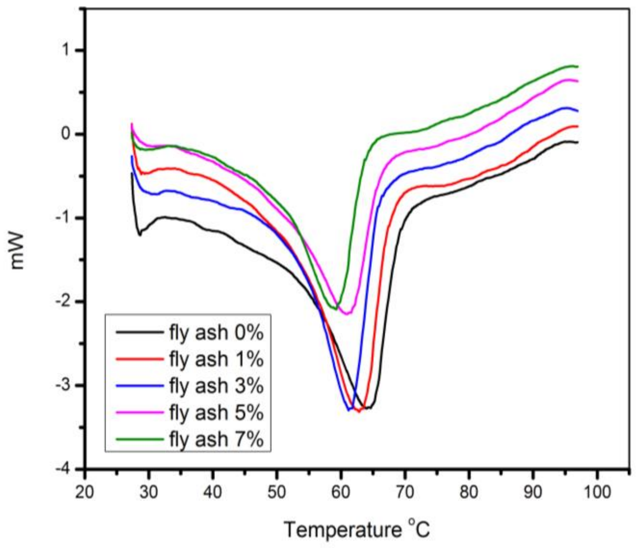


Figure 4. DSC thermograms of PEO:Na with different ratio of Fly ash (a) 0 %, (b) 1 %, (c) 3 %, (d) 5% and (e) 7%.

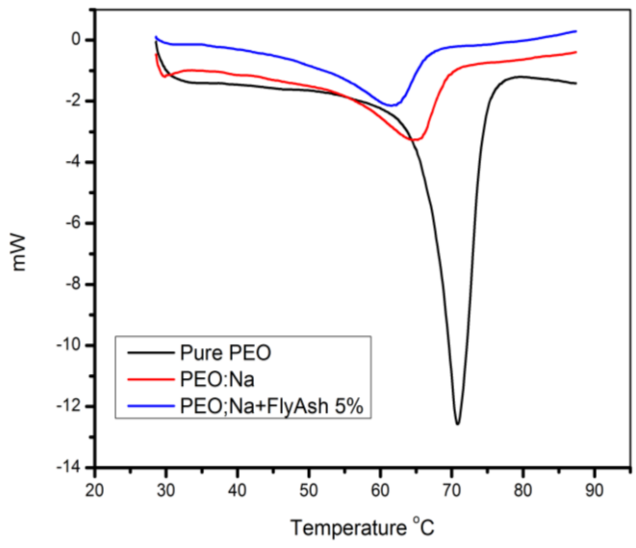


Figure 5. DSC thermograms of various solid polymer electrolytes pure PEO, PEO-NaClO$_4$ with EO: Na = 20 and PEO: Na + Fly Ash 5%

FTIR analysis was carried out to find out the interaction between PEO: Na and fly ash. FTIR spectrum in the range of 400-4000 cm^{-1} was shown in Figure 6. The peaks at the wavenumber of 800, 939, 1083 cm^{-1} were the interaction between PEO: Na with Fly Ash (with the main compound of SiO$_2$) (Shokri et al., 2009). The vibration of CH$_2$ in PEO chain was band observed in pure PEO at 2887, 1446, 1343-1366, 1297-1240, 960 and 843 cm^{-1}. The vibrational peak at 2935 cm^{-1}, 2938 cm^{-1}, 2921 cm^{-1} and 2923 cm^{-1} were assigned to asymmetric stretching of CH$_2$. The C-O-C stretching triplet observed in pure PEO at 1200-1000 cm^{-1}. The peak at 625 cm^{-1} was observed in the spectra of the PEO based SPE. The FTIR analysis gives us the information about the interaction between the polymer and salt in the polymer film (Kunteppa et al., 2011).

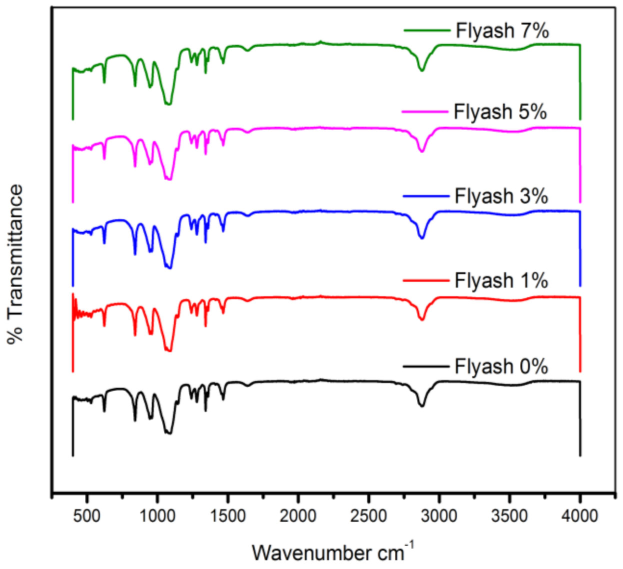


Figure 6. FTIR spectrum of PEO:Na and PEO:Na with different ratio of fly ash (a) 0 %, (b) 1 %, (c) 3 %, (d) 5% and (e) 7%.

Figure 7 shows the FTIR spectrum of pure PEO, PEO: Na, and PEO: Na + 5% Flyash at wavelength 500-700 cm-1. The peak at 625 cm^{-1} is a peak that indicates the presence of ClO_4^- functional group. Pure PEO shows flat spectrum without any peak appears at 625 cm^{-1}. PEO: Na from ClO_4^- appears, this indicates that the addition of a salt of $NaClO_4$ in PEO has become Na^+ and ClO_4^- ions. on the chart of PEO: Na + Fly Ash 5% ClO_4^- the peak slightly larger than PEO: Na. The peak on PEO: Na shows % transmittance is 60 while PEO: Na + Fly Ash 5% is 59. Fly Ash addition 5% indicates ionization of $NaClO_4$ more than PEO: Na without Fly Ash, so ion Na + in SPE is also increasing. The increasing Na^+ ion in the electrolytic polymer matrix provides an increase in the conductivity of the SPE by the addition of a 5% Fly ash filler (Mohamed et al., 2017).

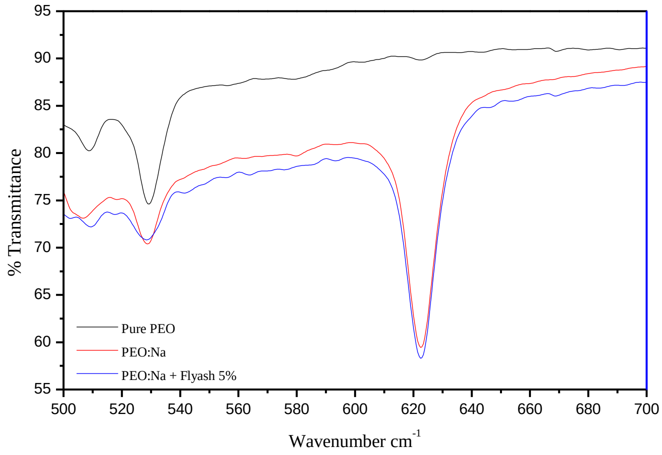


Figure 7. FTIR pattern of (a) pure PEO, (b) PEO:Na, and (c) PEO:Na + Fly Ash 5%.

The ionic conductivity of the samples was calculated by the equation:

$$\sigma = t/(A \times Rb)$$

where σ is the calculated ionic conductivity in S cm^{-1}, t is the thickness of the film in cm, Rb is the resistance in Ohm, and A is the cross-sectional area of the SS (Stainlessteel-Stainlessteel) electrode in cm^{-2}.

The bulk of resistance is obtained from the intercept of semicircle at the high-frequency side (1 MHz – 1 Hz) of the plot, with the real axis. As seen in Table 2 and Figure 8, the 5% fly ash – blended polymer electrolyte offers an even higher ionic conductivity, which is 2.123 x 10^{-4} S cm^{-1} at 60ºC compared to PEO-$NaClO_4$ and in Figure 8 the higher conductivity shows in log σ 3,7641 (S/cm). This is related to the higher crystallinity and amorphicity of the PEO host, which reported also by previous work (Ni'mah et al., 2015) (Lin et al., 2005).

Table 2. The Conductivity of PEO-Na film with varied fly ash concentration.

	PEO-Na	PEO-Na FlyAsh 1%	PEO-Na FlyAsh 3%	PEO-Na FlyAsh 5%	PEO-Na FlyAsh 7%
50°C	2,07 x 10^{-5}	2,94 x 10^{-5}	2,76 x 10^{-5}	8,49 x 10^{-5}	6,49 x 10^{-5}
60°C	5,31 x 10^{-5}	5,44 x 10^{-5}	1,82 x10^{-4}	2,12 x 10^{-4}	1,16 x 10^{-4}
70°C	5,44 x 10^{-5}	1,01 x 10^{-4}	1,12 x 10^{-4}	1,48 x 10^{-4}	1,48 x 10^{-4}
80°C	2,54 x 10^{-5}	5,69 x 10^{-5}	6,18 x 10^{-5}	1,45 x 10^{-4}	1,55 x 10^{-4}
90°C	6,18 x 10^{-5}	8,16 x 10^{-5}	8,61 x 10^{-5}	1,65 x 10^{-4}	1,59 x 10^{-4}

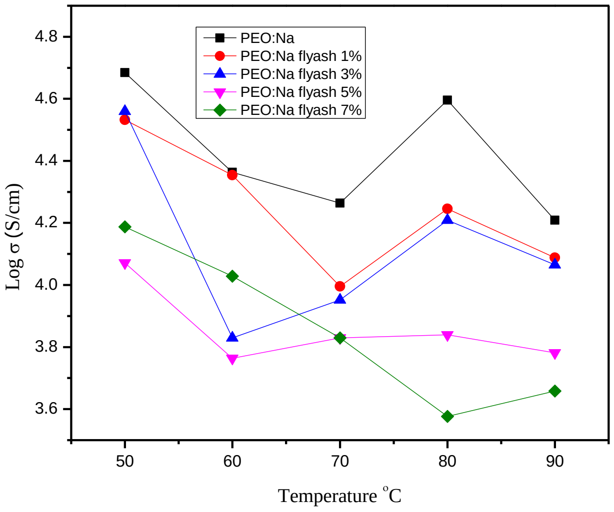


Figure 8. The influence of fly ash concentration (a) 0 %, (b) 1 %, (c) 3 %, (d) 5% and (e) 7% on PEO-Na film conductivity at varied temperature.

Apparently, conductivity enhancement below the melting point of the solid polymer electrolyte with fly ash the filler was a function of the filler concentration that influences the crystallinity and amorphocity of the film. As the filler concentration increase, the crystallinity of SPE decrease. The decrease in crystallinity, increase the flexibility of SPE film. Increasing flexibility of polymer chains makes the interaction among polymer chains increase and Na^+ mobility within the polymers film increase as well. The increase of Na^+ mobility makes the polymer conductivity increase. Thus, conductivity was influenced by crystallinity (Zhou, 2004).

CONCLUSION

Solid polymer electrolytes based on polyethylene oxide (PEO): $NaClO_4$ and fly ash as fillers were prepared by solution casting technique. The polymer electrolyte composite with a ratio of EO: Na = 20 and 5% fly ash filler produce electrolyte with maximum ionic conductivity at around 2.13 x 10^{-4} s cm^{-1} at 60ºC.

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