Perovskite Solar Cells with Binary Salt Based Gel Polymer Electrolyte

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***Abstract*—In this work, gel polymer electrolytes based poly(vinyl alcohol) (PVA) with different concentrations of tetrabutylammonium iodide (TBAI) and lithium iodide (LiI) salts have been prepared. The electrolyte conductivity at room temperature is observed to increase from 4.88 mS cm^{-1} for electrolyte with 17.02 wt.% PVA–13.93 wt.% TBAI–0.96 wt.% I_2–68.09 wt.% DMF (S1 electrolyte) to 6.47 mS cm^{-1} for electrolyte with 16.98 wt.% PVA–11.81 wt.% TBAI–2.09 wt.% LiI–1.21 wt.% I_2–67.92 wt.% DMF (S4 electrolyte). The conductivity increases from electrolyte S1 to S4 was attributed to the increase in the concentration of mobile ion. The increase in conductivity beyond the S4 electrolyte concentration is influenced by the mobility and diffusivity of charge carriers. All electrolytes prepared have been used in fabricating of methylammonium lead iodide ($MAPbI_3$) perovskite solar cells. The perovskite solar cell with S4 electrolyte shows the highest power conversion efficiency of 1.75% with open circuit voltage (V_{oc}) of 0.62 V and short circuit current density (J_{sc}) of 3.97 mA cm^{-2}.**

Keywords— Gel polymer electrolyte; electrical transport properties; perovskite solar cell; binary iodide salt.

I. INTRODUCTION

In recent year, perovskite solar cell (PSC) has become a concern for many researchers due to its ability to produce power conversion efficiency (PCE) up to 24.2% [1]. Perovskite materials have been used as photosensitizers because of their ability to convert light into electron charges [2-3]. Basically, the structure of perovskite materials used in solar cells is in the form of ABX_3. Here A is an organic cation (methylammonium or formamidinium ion), B is a metal cation (Pb or Sn ion) and X is halide anion (Cl, Br and I) [3]. Methylammonium lead iodide ($CH_3NH_3PbI_3$ or $MAPbI_3$) is widely used as photon absorber as it has large visible light absorption coefficient and direct band gap which able to generate high solar efficiency [4-5].

In PSC, spiro-OMeTAD and P3HT have been used by many researchers as hole transport medium (HTM) to transfer electrons from counter electrode to the perovskite materials. However, the cost of this material is ten times higher compared to gold or platinum. Polymer electrolyte is extensively used in dye sensitized solar cells (DSSCs) and revealed PCE up to 10% as well as low cost and easy to handle compared to HTM [6-7]. It is reported that the $CH_3CH_2NH_3PbI_3$ perovskite solar cells fabricated with a solid polymer electrolyte of 77.63 wt.% PEO–19.41 wt.% KI–2.96 wt.% I_2 revealed the efficiency of 0.75% under 1000 W m^{-2} light illumination [8]. Although the efficiency is low, this shows that polymer electrolytes have the potential to be used in perovskite solar cells as well in order to reduce the use of hole transport materials.

In this work, poly(vinyl alcohol) or PVA is used as a host polymer for gel polymer electrolyte (GPE). Dimethylformamide (DMF) was used as a solvent as well to keep the electrolyte in the gel form. It is reported that the DSSC fabricated with GPEs containing binary iodide salts increased the electron injection along with increasing electron transfer rate led to high J_{sc} as well as high PCE [9-10]. Hence, in this work tetrabutylammonium iodide (TBAI) and lithium iodide (LiI) salts were used as charge carriers in GPE. The effects of different TBAI and LiI salts concentration in GPE toward PSC performance have also been investigated.

II. EXPERIMENTAL

A. *Gel polymer electrolyte preparation*

PVA based gel polymer electrolytes were prepared using 0.5 g of poly(vinyl alcohol) (PVA) and 2.0 g of dimethylformamide (DMF). Different amounts of tetrabutylammonium iodide (TBAI) and lithium iodide (LiI) as listed in Table 1 were used so that the sum of both salts remained at 0.4091 g in all electrolytes. A small amount of Iodide (I_2) of mass equivalent to 10 mole% of the total number of mole of iodide salts were added to each composition.

Table 1. Compositions and designations of PVA-DMF-TBAI-LiI-I_2 gel polymer electrolyte system

Sample designation	TBAI : LiI (wt.% : wt.%)	TBAI (g)	LiI (g)	I_2 (g)
S1	100 : 0	0.4091	0.0000	0.0281
S2	95 : 5	0.3886	0.0205	0.0306
S3	90 : 10	0.3682	0.0409	0.0331
S4	85 : 15	0.3477	0.0614	0.0355
S5	80 : 20	0.3273	0.0818	0.0380
S6	75 : 25	0.3068	0.1023	0.0405

DMF in a glass bottle is added with the appropriate amount of TBAI and LiI. The mixture was stirred at 298 K for 1 h. The homogenized liquid electrolytes was then added with PVA and stirred continuously at 393 K for 4 h. The required amount of I_2 was then added into each gel and stirring continued until the gel reached room temperature

B. TiO_2 electrode preparation

The fluorine-doped tin oxide (FTO) glass was first spin coated with TiO_2 blocking layer that prepared by grinding 0.5 g TiO_2 (Degussa P-90) powder in 2.5 mL HNO_3 of pH=1 at 2350 rpm for 60 s. The coated glass was sintered at 723 K for 30 min and then allowed to cool to room temperature. The mesoporous TiO_2 layer was coated on the TiO_2 blocking layer by using doctor blade method. This mesoporous TiO_2 paste was prepared by grinding 0.5 g TiO_2 (Degussa P-25) powder with 2 mL HNO_3 (pH=1), 0.1 g surfactant and 0.1 g carbowax. The electrode was then sintered at 723 K for 30 min to produce the pores and left to cool to room temperature.

C. Perovskite solar cells (PSCs) fabrication

$MAPbI_3$ perovskite was prepared by spin coated a solution of 0.55 M lead iodide (PbI_2) in DMF on TiO_2 photoanode at 3000 rpm for 20 s. The electrode was then annealed on a hot plate at 373 K for 5 min. A solution of 0.044 M methylammonium iodide (MAI) in isopropanol was spin coated on PbI_2-TiO_2 electrode at 3000 rpm for 20 s and again annealed for 5 min at 373 K. A colour change from yellowish to dark brown was observed after the solution of MAI was added. PSCs with configuration of FTO/bl-TiO_2/meso-TiO_2/perovskite/GPE/Pt counter electrode were then fabricated and ready to be tested. Pt counter electrode was prepared by brushing the Plastisol (Solaronix) solution onto a cleaned FTO glass at 473 K and then sintered at 723 K for 30 min.

D. Impedance spectroscopy measurement

Impedance of GPEs have been measured using HIOKI 3532-50 LCR Hi-Tester in the frequency range between 50 Hz and 5 MHz at room temperature (298 K). The GPE was filled in a coin cell so that the electrolyte was placed between two stainless steel blocking electrodes of 2.01 cm^2 area. A graph of negative imaginary impedance (Z'') against real impedance (Z') was then plotted. The intercept of the plot with the real impedance axis reveal the value of bulk resistance, R. Equation below was used to calculate the conductivity, σ of the sample:

$$\sigma = \frac{d}{A \times R} \tag{1}$$

Here d is the sample thickness (0.26 cm) and A is the electrolyte/electrode contact area.

E. Photocurrent density-voltage (J-V) characteristics

The fabricated PSC were exposed under light illumination of 1000 W m^{-2} at room temperature. J-V characteristics of the PSC were carried out using Autolab potentiostat-galvanostat. From *J-V* plot, the fill factor, *FF* of the PSC was calculated using the following equation:

$$FF(\%) = \frac{J_{opt} V_{opt}}{J_{sc} V_{oc}} \times 100\% \tag{2}$$

Here, J_{opt} and V_{opt} are current density and voltage at maximum power output, respectively. J_{sc} is the short circuit current density. V_{oc} is the open-circuit voltage. The power conversion efficiency (PCE) of the cell was calculated using equation (3).

$$PCE(\%) = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100\% \tag{3}$$

Here, P_{in} is the total incident power density on to the cell.

III. RESULTS AND DISCUSSION

Fig. 1 shows the variation of ionic conductivity of PVA-TBAI-LiI-I_2-DMF GPEs system at room temperature (298K). It can be seen that the S1 electrolyte (containing 100 wt.% TBAI) conductivity is 4.88 mS cm^{-1}. When 5 wt.% of LiI salt is added and reduces the amount of 5 wt.% TBAI (S2 electrolyte), the conductivity increase to 5.55 mS cm^{-1}. The conductivity was observed gradually increase with increased LiI salt content in the electrolyte up to 25 wt.% of LiI salt which had been replaced by TBAI salt of 25 wt.% (S6 electrolyte) and gave the conductivity value of 6.47 mS cm^{-1}. The variation of the conductivity shown in Fig. 1 could be attributed to the increase/decrease in charge carriers density or/and mobility [11].

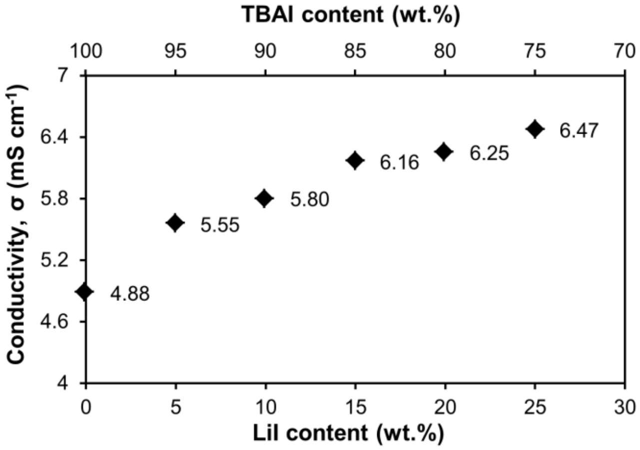

Fig. 1. Room temperature ionic conductivity of PVA-TBAI-LiI-I_2-DMF GPEs system.

In order to explain the conductivity variation obtained in Fig. 1, charges transport parameter which is the diffusion coefficient (D), mobility (μ) and charge carrier density (n) is calculated. Arof *et al.* [12] have formulated a method to determine the transport properties of charge carriers based on fitting the Nyquist plot obtained from impedance spectroscopy with appropriate equivalent circuit. The Nyquist plot obtained in this work consists of only tilted spike as shown in Fig. 2.

This type of Nyquist plot can be represents in equivalent circuit as a resistor that connected in series with constant phase element (CPE). The real (Z') and imaginary (Z'') impedance of the plot can be written as below:

$$Z' = R + \frac{\cos\left(\frac{\pi p}{2}\right)}{k^{-1}\omega^{p}} \quad (4)$$

$$Z'' = \frac{\sin\left(\frac{\pi p}{2}\right)}{k^{-1}\omega^{p}} \quad (5)$$

In equations (4) and (5), R is the bulk resistance of the electrolyte. p is the fraction of a right angle that is ($p\pi/2$), the angle between the inclined spike and the Z' axis. The inverse capacitance (k) is determined by trial and error until the fitted points quite accurately approximate the experimental Nyquist plot at the corresponding frequencies. ω is angular frequency corresponding to the minimum point in imaginary parts (Z''_{min}) (refer [11] for fitting method).

Using the corresponding values of R, p, k and ω obtained from the fitting, the values of D, μ and n of the charge carriers are calculated using the following equation:

$$D = D_o \exp\left\{-0.03[Ln(D_o)]^2 - 1.43[Ln(D_o)] - 14.50\right\} \quad (6)$$

$$\mu = \frac{eD_o \exp\left\{-0.03[Ln(D_o)]^2 - 1.43[Ln(D_o)] - 14.50\right\}}{k_b T} \quad (7)$$

$$n = \frac{\sigma k_b T}{e^2 D_o \exp\left\{-0.03[Ln(D_o)]^2 - 1.433[Ln(D_o)] - 14.50\right\}} \quad (8)$$

where

$$D_o = \frac{4k^4 d^2}{R^4 \omega^3} \quad (9)$$

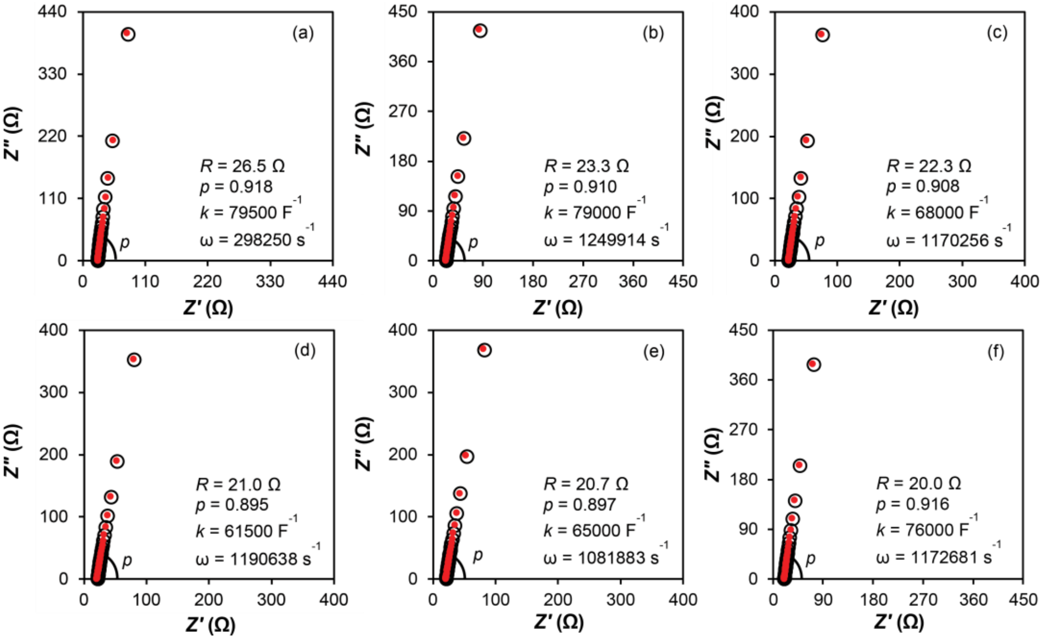

Fig. 2. Nyquist plot (o) and their corresponding fitted points (●) for (a) S1, (b) S2, (c) S3, (d) S4, (e) S5 and (e) S6 electrolytes.

In equations (8) and (9), k_b is the Boltzmann constant, T is the absolute temperature and d is the thickness of the sample. Fig. 3 shows the plot of D, μ and n of charge carriers for PVA based gel polymer electrolyte containing different TBAI and LiI salts ratios.

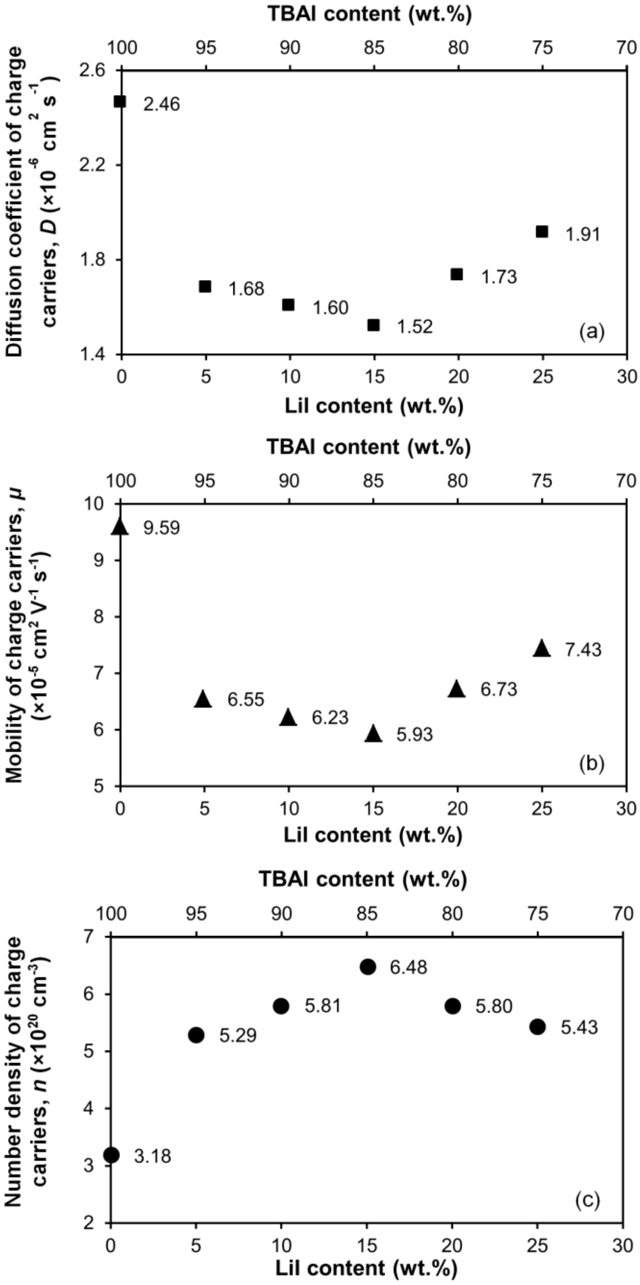

Fig. 3. Variation of (a) diffusion coefficient, (b) mobility and (c) number density of charge carriers of PVA-TBAI-LiI-I_2-DMF GPEs system.

From Fig. 3, it can be seen that the density charge carriers of the gel polymer electrolytes system increase continuously up to S4 electrolyte. The increase in n is attributed to the increase in number of ion dissociated as the amount of TBAI was replaced with LiI salt up to 15 wt.%. As more LiI salt is added, more free ions are form. The value of n is observed to decrease when more LiI salt replace the TBAI salt. The decrease in n is due to the increase of ion association. It is noted that the lattice energy of LiI salt is 757 kJ mol^{-1} [13] which is higher than TBAI salt of 513 kJ mol^{-1} [12]. High lattice energy difficult the salt to dissociate into free ions, thus increase the number of ion association as seen for GPE beyond S4 electrolyte when more LiI salt was added.

Referring to Fig. 3, it is noted that D and μ decrease as LiI salt content increase from 0 (S1 electrolyte) to 15 wt.% (S4 electrolyte). The decrease of D and μ may due to an increase in ions collusion between free ions in gel polymer electrolytes. This is because more free ions are formed as more LiI salts are added as shown in Fig. 3(c). This causes the collision between free ions to easily occur. Therefore the movement of free ions becomes slow, thus reduce their diffusivity and mobility. Beyond S4 electrolyte composition, D and μ were observed to increase. This is because n in the electrolyte become lesser. The collision between free ions is reduced resulting in the efficient movement of free ions. This led in increasing the D and μ of charge carriers in gel polymer electrolyte beyond S4 electrolyte concentration. Based on the results obtained, the σ increase from S1 to S4 electrolyte can be attributed to increase in n. Beyond S4 electrolyte composition, the conductivity of PVA–based gel polymer electrolyte was dominantly attributed by D and μ of charge carriers.

All electrolyte prepared in this work have been used as charge transport medium in perovskite solar cells (PSCs). The photocurrent density versus voltage plot of the cells is shown in Fig. 4. Table 2 listed the values of J_{sc}, V_{oc}, *FF* and *PCE* obtained from the *J-V* plot.

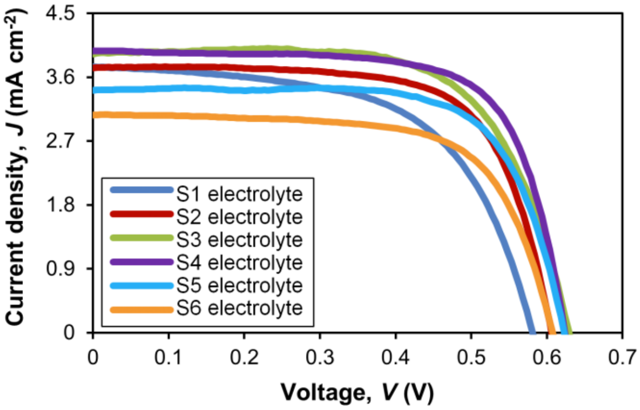

Fig. 4. *J-V* curve for perovskite solar cells fabricated with PVA-TBAI-LiI-I_2-DMF GPEs system.

Table 2. Values of J_{sc}, V_{oc}, *FF* and *PCE* for respectively GPE composition used in perovskite solar cells.

Sample	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	*PCE* (%)
S1	3.74	578	59.18	1.28
S2	3.74	603	69.35	1.56
S3	3.93	623	67.92	1.68
S4	3.97	628	70.81	1.75
S5	3.41	623	73.42	1.56
S6	3.08	608	67.70	1.27

It can be seen that the value of J_{sc} and *PCE* in Table 2 increased from 3.74 to 3.97 mA cm^{-2} and 1.28 to 1.75%, respectively with increasing LiI concentration in gel polymer electrolyte up to PSC with S4 electrolyte. When more than 15 wt.% LiI salt replaces TBAI salt in electrolyte composition, J_{sc} and *PCE* are decreased. The increase in J_{sc} may be attributed to the increase of electrons transfer rate from counter electrode to perovskite materials [14]. Number of free ions in gel polymer electrolytes is one of the key factors that increased the rate of redox mediator process. Referring to Fig. 3(c), n is observed to follow the same trends as J_{sc} and *PCE* as tabulated in Table 2. Large number of free I^-/I_3^- ions in gel polymer electrolyte increased the electron transfer rates from Pt counter electrode to $MAPbI_3$ perovskite materials. The decreasing of charge carrier density in gel polymer electrolyte sluggish the rate of electron transfer thus reduced the J_{sc} as well as *PCE*. The V_{oc} can be considered constant in all the PSC. Based on results obtained in this work, the *PCE* of perovskite solar cells was dominantly influence by the number density of charge carriers.

IV. CONCLUSIONS

Poly(vinyl alcohol) or PVA with different tetrabutylammonium iodide (TBAI) and lithium iodide (LiI) salts content in dimethylformamide (DMF) have been prepared and used as a medium in MAPbI3 perovskite solar cells. The increase in conductivity with increasing LiI salt content in gel polymer electrolyte up to electrolyte of composition 16.98 wt.% PVA–11.81 wt.% TBAI–2.09 wt.% LiI–1.21 wt.% I_2–67.92 wt.% DMF (S4 electrolyte) was attributed by number density of charge carriers. The conductivity increase beyond S4 electrolyte composition was dominantly influence by the increase in diffusion coefficient (D) and mobility of charge carriers (μ). Perovskite solar cell fabricated with S4 electrolyte revealed the highest power conversion efficiency of 1.75% which attributed by the highest charge carrier density in the electrolyte that help to enhance the rate of electron transfer. Based on this work, it is proved that polymer electrolyte is able to be used in perovskite solar cell.

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REFERENCES

[1] NREL Efficiency Chart. 2019 July 16, 2019]; Available from http://www.nrel.gov/pv/assers/images/efficiency_chart.jpg.

[2] K. Kojima, Y. Teshima, T. Shirai, J. Miyasaka, "Tsutomu Miyasaka Organo metal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells," Am. Chem. Soc., 131(17), pp. 6050-6051, 2009.

[3] N.-G. Park, "Perovskite solar cells: an emerging photovoltaic technology," Mater Today, 18(2), pp. 65-72, 2015.

[4] N.-G. Park, "Methodologies for high efficiency perovskite solar cells," Nano Convergence, 3(1), pp. 15, 2016.

[5] E. Mosconi, G. Grancini, C. Roldán-Carmona, P. Gratia, I. Zimmermann, M.K. Nazeeruddin, F. De Angelis, "Enhanced $TiO_2/MAPbI_3$ electronic coupling by interface modification with PbI2," Chem. Mater., 28(11), pp. 3612-3615, 2016.

[6] M.H. Buraidah, Shahan Shah, L.P. Teo, Faisal I.Chowdhury, M.A. Careem, I. Albinsson, B.-E. Mellander, A.K. Arof, “High efficient dye sensitized solar cells using phthaloylchitosan based gel polymer electrolytes,” Electrochim. Acta, 245, pp. 846-853, 2017.

[7] F. Bella, "Polymer electrolytes and perovskites: lights and shadows in photovoltaic devices," Electrochim. Acta, 175, pp. 151-161, 2015

[8] Rahul, B. Bhattacharya, P.K. Singh, R. Singh,Z.H. Khan, "Perovskite sensitized solar cell using solid polymer electrolyte," Int. J. Hydrogen Energy, 41(4), pp. 2847-2852, 2016.

[9] M.A.K.L. Dissanayake, C.A. Thotawatthage, G.K.R. Senadeera, T.M.W.J. Bandara, W.J.M.J.S.R. Jayasundara,B.-E. Mellander, "Efficiency enhancement in dye sensitized solar cells based on PAN gel electrolyte with $Pr_4NI+MgI_2$ binary iodide salt mixture," J. Appl. Electrochem., 43(9), pp. 891-901, 2013.

[10] Y. Shi, Y. Wang, M. Zhang, X. Dong, "Influences of cation charge density on the photovoltaic performance of dye-sensitized solar cells: lithium, sodium, potassium, and dimethylimidazolium," Physical Chemistry Chemical Physics, 13(32), pp. 14590-14597, 2011.

[11] A.K. Arof, S. Amirudin, S.Z. Yusof,I.M. Noor, "A method based on impedance spectroscopy to determine transport properties of polymer electrolytes," Phys. Chem. Chem. Phys., 16(5), pp. 1856-1867, 2014.

[12] A.K. Arof, I.M. Noor, M.H. Buraidah, T.M.W.J. Bandara, M.A. Careem, I. Albinsson, B.-E. Mellander, “Polyacrylonitrile gel polymer electrolyte based dye sensitized solar cells for a prototype solar panel. Electrochim. Acta, 251, pp. 223-234, 2017.

[13] D.L. Reger, S.R. Goode,D.W. Ball, Chemistry: principles and practice: Cengage Learning, 2009.

[14] J. Bisquert, F. Fabregat-Santiago, I. Mora-Seró, G. Garcia-Belmonte,S. Giménez, "Electron lifetime in dye-sensitized solar cells: theory and interpretation of measurements," J. Phys. Chem. C, 113(40), pp. 17278-17290, 2009