Response surface method (RSM) for optimization of ionic conductivity of membranes polymer electrolyte poly (vinylidene fluoride) (PVDF) with polyvinyl pyrrolidone (PVP) as pore forming agent

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Abstract. The Membranes Polymer Gel Electrolyte (MPGEs) based poly (vinylidene fluoride) (PVDF) was prepared by a phase inversion method using polyvinyl pyrrolidone (PVP) as a pore-forming agent and N, N-dimethyl acetamide (DMAc) as a solvent and water as non solvent. The membranes were then soaked in 1 M lithium hexafluorophosphate (LiPF6) in ethylene carbonate (EC) / dimethyl carbonate (DMC) / Diethyl carbonate (DEC) (4:2:4 vol%) solution in order to prepare polymer electrolyte membranes. The MPGEs PVDF/PVP/Nanoclay was applied using central composite design (CCD) experimental design to obtain a quantitative relationship between selected membranes prepared parameters namely (PVDF, PVP as pore forming agent and nanoclay filler concentration) and Ionic conductivity MPGEs. The model was used to find the optimum ionic conductivity from polymer electrolyte membranes. The polymer electrolyte membranes show good ionic conductivity on the order of $6.3 - 8.7 \times 10^{-3}$ S cm$^{-1}$ at the ambient temperatures. The ionic conductivity tended to increase with PVP and nanoclay concentration and decrease with PVDF composition. The model predicted the maximum ionic conductivity of $8.47 \times 10^{-3}$ S cm$^{-1}$ when the PVDF, PVP and nanoclay concentration were set at 8.01 %, 8.04 % and 10.12%, respectively. The first section in your paper.

1. Introduction

Lithium ion battery has many excellent properties such as high working voltage, high energy density, long cycle life, low self-discharge rate, low pollution, no memory effect [1]. However, the use of liquid electrolytes which has highly reactive properties in conventional lithium ion batteries will increase their internal pressure in the cell and lead to unsafe conditions. It conditions will also lead to a leakage problem. The use of polymer gel electrolyte instead of liquid electrolyte is an effective way to overcome the weakness of the liquid electrolyte because GPE consisting of a polymer matrix, plasticizer and additives.

The gel polymer electrolyte membrane with a pore size of nanometers up to micrometers have good electrochemical properties when soaked in an organic solution lithium salts. The solution containing sufficient charge carrier as a medium for ion mobility. Ionic conductivity of polymer electrolyte membranes depends on not only the polymer type, but also pore size, porosity, tortuosity, and pore distribution. Its characteristic is determined by processing method.

Phase inversion is a technology that is widely used in the manufacturing of porous polymer electrolyte. The porous polymer electrolyte with pore size within micro-meter range prepared by phase inversion can entrap large amounts of fluid electrolyte which increase the ratio of...
uptake and improves ionic conductivity [2]. However, the abundant micro-pores and absorption of liquid electrolyte will weaken the mechanical strength of the polymer matrix. Adding some inorganic particles such as ZrO₂, TiO₂, MgO into the polymer matrix was confirmed some effects in solving this problem [3–7].

Poly (vinylidene fluoride) or Poly (vinylidene difluoride) (PVDF) is one of the most promising host matrix for the polymer electrolyte because it has many excellent properties such as good chemical resistance, high dielectric constant, and thermal stability [8–10]. The use of pore-forming agent can enhance the ionic conductivity of membrane at room temperature by improving the pore structure within the membranes. Some literature have reported that the polyvinyl pyrrolidone (PVP) can be used as a pore-forming agent to improve polymer electrolyte ionic conductivity [11–13]. Xiao and his coworkers explored the effect of PVP, on the properties of PVDF based gel polymer electrolyte. The result showed that PVP can be used as pore forming agents for PVDF polymer. Further, the results showed that the physicochemical and electrochemical properties of electrolyte with PVP, indicate a promising pore forming agent for polymer electrolyte in rechargeable lithium-ion polymer battery[14]. The polymer electrolyte has a weak mechanical strength, because of the plasticization of the entrapped liquid electrolyte in the polymer matrix. Several studies have been performed to balance the ionic conductivity at room temperature with its mechanical strength, such as by adding inorganic particles (ZrO₂, Al₂O₃, TiO₂, and MgO) into a polymer matrix [15,16].

The addition of Al₂O₃ nanoparticles can also increase the ionic conductivity, because Lewis acidbase effects of the - OH groups can weaken the interaction between the Li⁺ ion and F atoms of the polymer chain as has been shown by Zhao [17]. Li et al. successfully prepared a P(VDF-HFP) polymer electrolyte with urea as pore-forming agent and nano-SiO₂ as additives. Their research found that urea and nano-SiO₂ can improve the performance of polymer electrolyte, such as ionic conductivity at room temperature, mechanical strength, electrochemical stability, lithium-ion transference number, and interfacial properties. The performance of Battery lithium ion cell assembled with GPEs also demonstrated excellent properties[18].

Design of experiment (DOE) method is a statistically based approach that creates the numerical model, determines the importance of parameters, and optimizes a process . In this case, response surface methods (RSM) suitable to be applied because of its simplicity and its ability to consider the interaction between the parameters [19,20]. The RSM is a straightforward strategy that might consider collaborations around the parameters. RSM consists of five steps: preference of requisite parameters and their levels, backbone of necessary tests by suitable design, performing experiments and regression analysis, computation of optimum operating condition, and validation of the model [21–24]. The analyses for optimizing the PVDF/PVP ionic conductivities were decided by the Central composite design (CCD) method. The PVDF, PVP and Nanoclay concentration were selected as influential parameters. The ionic conductivity was chosen as response.

The purpose of this study is to investigate the quantitative relationship among three parameters, i.e., PVDF, PVP and nanoclay concentration and their influence on ionic conductivity of MPGEs using the method of RSM. The Central Composite Design (CCD) used in this testing performed to get the optimal parameters values, which resulted the maximum ionic conductivity of MPEG, in the quadratic model with three levels for each parameter.

2. Experimental
2.1 Materials
PVDF (Sigma Aldrich , MW 534,000) was used as polymer matrix in this work. Polyvinyl pyrrolidone (PVP) with 25,000 g/mol molecular weight from Merck were used as pore forming
agents in the preparation processes of GPEs. N,N-Dimethylacetamide (A.R., DMAc) was used as solvent directly without further purification and octadecylamine-modified montmorillonite nanoclay (MMT, SigmaAldrich) was used as filler. The electrolyte solution of LiPF$_6$ in solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) 1 M lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate (EC)/dimethyl carbonate (DMC)/Diethyl carbonate (DEC) (4:2:4 vol.% solution was supplied by MTI Company.

2.2 Membrane preparation
The nano-clay particles (10% wt of PVDF) were mixed with DMAc solvent (2000 rpm, 30°C) for 2 h. Amount of PVDF was dissolved in dimethylacetamide (DMAC) under continuous stirring for 4 h at 45°C with the ratio with DMAC of 8-12. PVP powder (4 - 10% wt of PVDF) were then added to the above solution, and kept for 4 h. The solution mixture was cast using an automatic film coater (Adjustable Doctor Blade - MSK-AFA-II, MTI corp). In this experiment, the casting thickness was set to be 250 µm. The membranes were then immediately soaked in deionized water at room temperature for 48 h. The membranes were dried in the air at room temperature for 24 h. The resultant membrane was vacuum dried at 60°C for 12 h and transferred to a dry box at 30°C (H$_2$O level < 10 ppm).

2.3 Ionic conductivity measurement
PVDF/PVP/Nanoclay membrane gel electrolytes were prepared by soaking the membrane in the liquid electrolyte, 1 M LiPF$_6$ in (EC) / (DMC) / (DEC) (4:2:4 % vol), MTI Corp. The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS). The samples were measured in coin cells CR-2032, where the gel membranes activated with liquid electrolyte were sandwiched between two stainless steel electrodes. Impedance data were obtained with Hioki 3532-50 LCR in the frequency range 50 Hz to 1 MHz at 25°C. The ionic conductivity was calculated from (1):

$$\sigma = \frac{1}{(R_b \times A)} \text{[in mS cm}^{-1}]$$  \hspace{1cm} (1)

where $\sigma$ is the ionic conductivity, $R_b$ is the bulk resistance (Ω), $l$ is the thickness (cm) of the membrane separator, and $A$ (cm$^2$) is the area of the stainless steel electrode. $R_b$ was obtained using the high frequency intercept on the real axis. The effective area was determined by the circular stainless steel electrodes, and the thickness was around 300 µm.

2.4 Response Surface Method
To examine the relationship between response (Y) and independent variables, and optimizing the value variables to predict the maximum value the response in this research used RSM method. Central Composite Design (CCD) is an advantageous design for sequential experiments. Therefore, CCD was applied to determine the effect of operational variables on the ionic conductivity in this work.

3. Results And Discussions
3.1 Ionic conductivity study
Ionic conductivity of the electrolyte membrane depends on the number of ion carriers and ion mobility. The concentration of dissolved ions will affect the effective number of ion carriers. While the mobility of the polymer chain segments will facilitate the mobility of ions in the polymer electrolyte. A membrane that has a high absorption liquid electrolyte having a structure are fully interconnected porous. The process of absorption takes place rapidly, and maximum electrolyte absorption will be reached in just a few minutes. The membrane porosity, which
absorbs the liquid electrolyte and the gelation of the membrane, is important factor that influences electrolyte absorption [23].

| No. | PVDF (ratio with DMAc) | PVP (%wt PVDF) | Nano clay (%) | Ionic conductivity $\times 10^{-3}$ S cm$^{-1}$ |
|-----|------------------------|----------------|---------------|---------------------------------------------|
|     | Actual values | Coded values | Actual values | Coded values | Actual values | Coded values | Exp | Calculated from the model |
| 1   | 8           | -1           | 4             | -1           | 4            | -1           | 6.6130 | 6.652                   |
| 2   | 8           | -1           | 4             | -1           | 12           | 1            | 8.0101 | 7.792                   |
| 3   | 8           | -1           | 10            | 1            | 4            | -1           | 7.9609 | 7.761                   |
| 4   | 8           | -1           | 10            | 1            | 12           | 1            | 8.2235 | 8.136                   |
| 5   | 12          | 1            | 4             | -1           | 4            | -1           | 6.3475 | 6.365                   |
| 6   | 12          | 1            | 10            | 1            | 12           | 1            | 7.5737 | 7.505                   |
| 7   | 12          | 1            | 10            | 1            | 4            | -1           | 7.1173 | 7.474                   |
| 8   | 12          | 1            | 10            | 1            | 12           | 1            | 7.9547 | 7.761                   |
| 9   | 6.63641     | -1.68179     | 7             | 0            | 8            | 0            | 8.4756 | 8.712                   |
| 10  | 13.36359    | 1.68179      | 7             | 0            | 8            | 0            | 8.3801 | 8.229                   |
| 11  | 10          | 0            | 1.95462       | -1.68179     | 8            | 0            | 6.2372 | 6.344                   |
| 12  | 10          | 0            | 12.04538      | 1.68179      | 8            | 0            | 7.5806 | 7.566                   |
| 13  | 10          | 0            | 7             | 0            | 1.27283      | -1.68179     | 6.5162 | 6.363                   |
| 14  | 10          | 0            | 7             | 0            | 14.72717     | 1.68179      | 7.3890 | 7.637                   |
| 15  | 10          | 0            | 7             | 0            | 8            | 0            | 8.0285 | 8.026                   |
| 16  | 10          | 0            | 7             | 0            | 8            | 0            | 8.0408 | 8.026                   |
| 17  | 10          | 0            | 7             | 0            | 8            | 0            | 8.0285 | 8.026                   |
| 18  | 10          | 0            | 7             | 0            | 8            | 0            | 8.0469 | 8.026                   |
| 19  | 10          | 0            | 7             | 0            | 8            | 0            | 7.9978 | 8.026                   |
| 20  | 10          | 0            | 7             | 0            | 8            | 0            | 8.0347 | 8.026                   |

The EIS results show a sloping straight line, representation of the electrolyte / electrode double layer capacitance behavior observed in the entire frequency evaluation range. It can be concluded that there is only a small contribution to the resistance of the resistance boundary total. Intercept of a straight line is a bulk resistance of the electrolyte (Rb). The resultant polymer electrolyte composed
of three parts: (1) Solid polymer, (2) partially amorphous swelling membranes, and (3) a liquid electrolyte enclosed in the membrane pores.

Figure 1. Effect of process parameters on ionic conductivity of PVDF/PVP/Nanoclay polymer electrolyte. a). PVDF concentration. b). PVP concentration. c). Nanoclay concentration. The black lines indicate the 95% confidence level.
Two ionic conduction mechanisms occur in PGE: one is the fast conduction along the liquid electrolyte and the other is slower conduction in swelling polymer. The overall ionic conductivity of the polymer electrolyte is strongly influenced by the electrolyte liquid phase. The amount of liquid electrolyte that is adsorbed in the porous of PGE influences more ionic conductivity. Meanwhile its higher conductivity than the solution bounded in the swollen phase of porous polymer is observed.

The effects each parameter on ionic are shown in Figure 1. As shown in Figure 1(a), ionic conductivity versus the content of nanoclay when PVP and PVDF concentration was maintained at 8 (wt% PVDF) and 1: 9 (ratio PVDF with DMAc), the increased in ionic conductivity is observed as nanoclay filler was added until reached a maximum conductivity (8.476 mS cm⁻¹) at 8 wt% PVP. However, beyond this amount it tended to decrease. Several researches reported that lewis acid base interactive between particle site on the surface and the electrolyte could be the reason. Association between filler and polymer chain have been same reason. The higher ionic conductivity (8.476 mS cm⁻¹ from Figure 1(a)) of PVDF/PVP/Nanoclay membrane suggested that membranes contained more individual nanoclay filler than its intercalated assemblies. The primary reasons for the enhancement of ionic conductivity have been reported as the Lewis acid–base interactions between the functional group located on the surface of clay platelets and the electrolyte polar groups, and association between the filler particle and the polymer chains [25–27]. There were two distinct stages of liquid electrolyte adsorption in membranes with porous structure. The first, it filled the porous of membrane, next the electrolyte penetrated polymer chain resulted swollen phase amorphous. In Figure 1(b), it is observed that, at constant total polymer concentration, the ionic conductivity of the membranes decreased with increasing PVDF composition; this is due to the decrease in solution viscosity with increasing PVDF composition.

In order to investigate the effect of PVP on the properties of the polymer electrolyte, the ionic conductivity of polymer electrolyte based on the PVP and PVDF was measured as a function of PVP content. Figure 1(c), shows the ionic conductivity versus the content PVP. The ionic conductivity increased with increasing PVP content until reached its maximum value at PVP = 7 wt%. Beyond this value it decreased. This is related to the pore volume of the polymer film. With PVP content increase, the pore volume and the electrolyte uptake also increase, so the conductivity of the polymer electrolyte also increases [12]. The results showed the membranes pore structure makes ion pass easily between the electrodes. As compared to the value of ionic conductivity in the electrolyte solution LiPF₆ is 10.5 mS cm⁻¹ (MTI SDS).

3.2 Response surface development

To evaluate the full quadratic response surface model from experimental design, an analysis of variance (ANOVA) was used. The result is presented in Table 2. From the test of significant model in this table, P values of the model <0.0001 indicates that the model is significant. Exactly between the data and model indicated by R² = 0.9587. The fitted second-order model for ionic conductivity was:

$$Y = + 6.55256 \times 10^{-03} - 8.46438 \times 10^{-04} A + 9.22844 \times 10^{-04} B + 5.07913 \times 10^{-04} C - 8.54167 \times 10^{-06} A B + 6.09375 \times 10^{-06} A C - 1.59375 \times 10^{-05} B C + 3.92836 \times 10^{-05} A^2 - 4.20555 \times 10^{-05} B^2 - 2.26618 \times 10^{-05} C^2$$

where Y is variable response, A, B, and C are the values of parameter (PVDF concentration, PVP concentration, and Nanoclay concentration), respectively. Significance of the factors was analyzed in order to understand the level of influence of each parameter. The parameter A (PVDF), B (PVP) and C (Nanoclay) are significant as they have P values of less than 0.0001, respectively. The interaction terms AB and AC have a large P value of 0.4719 and 0.4932 indicating that this term is insignificant. The other interaction factor BC and the second-order terms A², B² and C² have small P values (<0.0001).
Eliminating the insignificant terms will enhance the efficiency of the model. After removing insignificant parameters in the model (AB and AC), the modified equation in uncoded variables, it is given by Eq. 3

\[ Y = +6.66297 \times 10^{-3} - 8.57480 \times 10^{-4} \times A + 8.37427 \times 10^{-4} \times B + 5.68851 \times 10^{-4} \times C - 1.59375 \times 10^{-5} \times BC + 3.92836 \times 10^{-5} \times A^2 - 4.20555 \times 10^{-5} \times B^2 - 2.26618 \times 10^{-5} \times C^2 \]  

Table 2. Estimated regression coefficients for the quadratic polynomial model and the analysis of variance for the experimental results.

| Source         | Sum of Square | dF | Mean Square | F value | p-value | Prob>F |
|----------------|---------------|----|-------------|---------|---------|--------|
| Model          | 8.717E-006    | 9  | 9.685E-007  | 25.76   | <0.0001 |        |
| A-PVDF         | 2.817E-007    | 1  | 2.817E-007  | 7.49    | 0.0209  |        |
| B-PVP          | 1.804E-006    | 1  | 1.804E-006  | 47.99   | <0.0001 |        |
| C-clay         | 1.960E-006    | 1  | 1.960E-006  | 52.13   | <0.0001 |        |
| AB             | 2.101E-008    | 1  | 2.101E-008  | 0.56    | 0.4719  |        |
| AC             | 1.901E-008    | 1  | 1.901E-008  | 0.51    | 0.4932  |        |
| BC             | 2.926E-007    | 1  | 2.926E-007  | 7.78    | 0.0191  |        |
| A^2            | 3.558E-007    | 1  | 3.558E-007  | 9.47    | 0.0117  |        |
| B^2            | 2.065E-006    | 1  | 2.065E-006  | 54.92   | <0.0001 |        |
| C^2            | 1.895E-006    | 1  | 1.895E-006  | 50.40   | <0.0001 |        |
| Residual       | 3.759E-007    | 10 |             |         |         |        |
| Lack of Fit    | 179.4407      | 5  |             |         |         |        |
| Pure Error     | 2.083E-009    | 5  |             |         |         |        |
| Cor Total      | 9.093E-006    | 19 |             |         |         |        |
| Std. Dev.      | 1.939E-004    |    | R^2         | 0.9587  |         |        |
| PRESS          | 2.952E-006    |    | Adj R^2     | 0.9214  |         |        |
| Pred R^2       |               |    |             | 0.6753  |         |        |

Based on the ANOVA results for this modified model (Table 3), the significant terms in model can be shown from the low of P values in the new model. The terms number in the model will always increase as R^2. Hence, smaller R^2 values is thought for the new model, for the sake of smaller the terms.

In Table 1, the ionic conductivity counted by the modified model (Eq. 3) is presented. Figure. 2 shows the plotted of the experimental versus the predicted of ionic conductivity from the modified model. The experimental and models values around the range of parameters under evaluation suggests that the results were well verified.

Making use of the model, the maximum ionic conductivity is equal to 8.47 mS.cm^{-1} corresponding to the test in Table 1. The model predicted the maximum ionic conductivity when the PVDF concentration set at 8.01 %, the PVP concentration set at 8.04 wt.%, and the nanoclay composition set at 10.12 wt.%. Wang produced the polymer electrolyte based on poly(vinylidene fluoride), PVDF, poly(ethylene glycol), PEG, and Li-exchanged vermiculite (Li-VMT) [28]. The maximum ionic conductivity achieved in their work for the membranes was 4.2 x 10^{-3} S.cm^{-1}. Xiao et al. prepared the
poly(vinylidene fluoride – co - hexa fluoropropylene) (PVDF-HFP) - based gel polymer electrolytes (GPEs) with polyvinylpyrrolidone (PVP) and urea as a pore forming agent by phase inversion method [14].

Table 3 Statistical parameters obtained from ANOVA for ionic conductivity

| Source | Sum of Square | dF | Mean Square | F value | p-value Prob>F |
|--------|---------------|----|-------------|---------|----------------|
| Model  | 8.677E-006    | 7  | 9.093E-006  | 35.76   | < 0.0001       |
| A-PVDF | 2.817E-007    | 1  | 2.817E-007  | 8.13    | 0.0146         |
| B-PVP  | 1.804E-006    | 1  | 1.804E-006  | 52.05   | < 0.0001       |
| C-clay | 1.960E-006    | 1  | 1.960E-006  | 56.53   | < 0.0001       |
| BC     | 2.926E-007    | 1  | 2.926E-007  | 8.44    | 0.0132         |
| A²     | 3.558E-007    | 1  | 3.558E-007  | 10.27   | 0.0076         |
| B²     | 2.065E-006    | 1  | 2.065E-006  | 59.56   | < 0.0001       |
| C²     | 1.895E-006    | 1  | 1.895E-006  | 54.66   | < 0.0001       |
| Residual | 4.159E-007 | 12 |             |         |                |
| Lack of Fit | 141.89 | 7  |             |         |                |
| Pure Error | 2.083E-009 | 5  |             |         |                |
| Cor Total | 9.093E-006 | 19 |             |         |                |

Std. Dev. 1.862E-004 R² 0.9543
PRESS 1.858E-006 Adj R² 0.9276
Pred R² 0.7957
The measured ionic conductivity at room temperature was $2.212 \times 10^{-3}$ S.cm$^{-1}$ for PVP pore forming and $2.823 \times 10^{-3}$ Scm$^{-1}$ for urea pore forming. Figures 3-5 show the interaction of variables and the optimum level of each parameter for maximum ionic conductivity. The ionic conductivity with different nanoclay and PVP contents at PVDF (ratio with DMAc) 1:10 is presented in Figure 3. It is clear that the nanoclay filler has positive effect on the ionic conductivity. As nanoclay increases.

**Figure 2.** Plot of model predicted ionic conductivity against experimental ionic conductivity
from 4 to 12 (%wt PVDF), the ionic conductivity increases from $6.23 \times 10^{-3}$ S. cm$^{-1}$.

**Figure 3.** Response Surface and contour plot for different PVP and Nanoclay content at PVDF ratio

**Figure 4.** Response Surface and contour plot for different Nanoclay and PVDF (ratio with DMAc) at PVP 8 %wt PVDF
Figure 5. Response surface and contour plot for different PVP and ratio PVDF with DMAc at Nanoclay 10% wt PVDF

Figure 4 shows the 3D response surfaces and contour plots as a function of nanoclay and PVDF concentration, while the PVP content was kept constant (8 %wt PVDF). The ionic conductivity increases with nanoclay content. The ionic conductivity of PVDF membranes decreases as the PVDF concentration is away from 4 (ratio with DMAc). An interaction between the two mentioned parameters can be noticed in these figures. Figure 5 shows the effect of PVDF and PVP content on ionic conductivity at constant nanoclay on content of 10 (%wt PVDF). The decrease in the PVDF concentration and the increase in PVP content lead to higher ionic conductivity. Based on the response surface plot shown in Figure 5, applying high PVP content and low PVDF concentration results in the maximum ionic conductivity.

4. Conclusions
The polymer electrolyte membranes were prepared by phase inversion method. Here PVDF concentration, PVP and Nanoclay concentration were chosen as parameter with ionic conductivity as a response variable. To obtain the maximum ionic conductivity Central Composite Design (CCD) as a method of RSM was used. For validating the model was investigated by analysis of variance (ANOVA) results. The ionic conductivity of the MPEGs polymer electrolyte increased as PVP and nanoclay concentration were increased. On the contrary the PVDF decreased concentration resulted in the decrease in ionic conductivity, as resulted from the higher uptake of the electrolyte solution in the membranes modified with pore forming agents and filler.

Acknowledgements
This work has been financially supported by the Ministry of Research, Technology and Higher Education (Kemenristekdikti) for Hibah PUPT 2016, Grant number 353 /UN27.21/PN/2016. Endah R Dyartanti is thankful to the Sebelas Maret University for the scholarship doctoral program. The authors also thankfully acknowledge to The Center for Science and Technology Advanced Materials, National Nuclear Energy Agency Indonesia for helpful and assistance to this experiment.
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