

**THE EFFECT OF  $\text{LiClO}_4$  CONCENTRATION ON 3D PRINTED  
POLYURETHANE ACRYLATE GEL POLYMER  
ELECTROLYTES FABRICATED VIA STEREOLITHOGRAPHY**

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**UNIVERSITI SAINS ISLAM MALAYSIA**

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POLYURETHANE ACRYLATE GEL POLYMER ELECTROLYTES  
FABRICATED VIA STEREO LITHOGRAPHY**

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## AUTHOR DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

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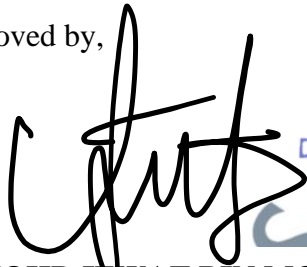
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## APPROVAL FOR SUBMISSION

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## ABSTRAK

Untuk memenuhi permintaan bateri berprestasi tinggi dan padat untuk elektronik mudah alih, percetakan 3D boleh dimanfaatkan untuk meningkatkan prestasi elektrolit polimer. Kerja ini menyediakan kaedah fabrikasi baharu untuk elektrolit polimer gel (GPEs) melalui penyepaduan pencetakan 3D stereolitografi (SLA) ke dalam proses fabrikasi tanpa mengurangkan prestasi GPEs. GPEs telah dibuat dengan melarutkan kepekatan litium perklorat ( $\text{LiClO}_4$ ) yang berbeza (0-25 wt.%) ke dalam larutan poliuretana akrilat (PUA) dan dimetilformamida (DMF), kemudian dicetak menggunakan kaedah SLA.

Ciri-ciri elektrik, morfologi dan terma GPEs dikaji melalui spektroskopi impedans elektrokimia (EIS), inframerah transformasi Fourier (FTIR), analisis pembelauan sinar-X (XRD), analisis termogravimetrik (TGA), kalorimetri pengimbasan pembezaan (DSC) dan pengimbasan mikroskop elektron (SEM). GPEs bercetak 3D mempamerkan kekonduksian ionik yang tinggi pada  $1.24 \times 10^{-3} \text{ S cm}^{-1}$  pada kepekatan  $\text{LiClO}_4$  yang rendah (10 wt.%). Hasilnya adalah selaras dengan bilangan ion bebas dan pecahan amorf yang ditentukan oleh penyahkonvolusian FTIR dan XRD kerana kedua-duanya menunjukkan nilai tertinggi pada 10 wt.%  $\text{LiClO}_4$ . Selain itu, penambahan  $\text{LiClO}_4$  ke dalam matriks polimer GPEs menyebabkan pergeseran dalam kumpulan berfungsi uretana, eter, dan karbonil. GPE 3D adalah stabil dari segi haba sehingga mencapai suhu sekitar 300 °C.

Memandangkan 10 wt.% sampel mempunyai prestasi terbaik, formulasi untuk 10 wt.% telah digunakan dalam membuat GPEs struktur 3D untuk menguji kebolehcetakannya yang merupakan ciri terpenting untuk pencetakan 3D. Formulasi tersebut berjaya dicetak kepada tiga reka bentuk berbeza; struktur sarang lebah, *interdigated* dan *scaffold* yang menunjukkan bahawa penyepaduan pencetakan 3D ke dalam fabrikasi GPEs telah berjaya. Keupayaan untuk membina struktur 3D elektrolit adalah penting kerana ia boleh meningkatkan prestasi bateri dengan ketara dengan menyediakan kawasan sentuhan yang lebih besar dengan elektrod.

## ABSTRACT

To address the demand for high-performance and compact batteries for portable electronics, 3D printing could be leveraged to enhance the polymer electrolytes performance. This work provides a new fabrication method for gel polymer electrolytes (GPEs) through the integration of stereolithography (SLA) 3D printing into the fabrication process while maintaining the GPEs performance. The GPEs were fabricated by dissolving different lithium perchlorate ( $\text{LiClO}_4$ ) concentrations (0-25 wt.%) into polyurethane acrylate (PUA) and dimethylformamide (DMF) solution, printed using the SLA method, and then studied the impact of  $\text{LiClO}_4$  towards the GPEs performance.

The electrical, morphological, and thermal characteristics of the GPEs were characterized through Electrochemical impedance spectroscopy (EIS), Fourier transform infrared (FTIR), X-ray diffraction analysis (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscope (SEM). The 3D printed GPEs exhibited high ionic conductivity at  $1.24 \times 10^{-3} \text{ S cm}^{-1}$  at low  $\text{LiClO}_4$  concentration (10 wt.%). The result was in line with the number of free ions and amorphous fraction determined by FTIR deconvolution and XRD respectively as both showed the highest value at 10 wt.%  $\text{LiClO}_4$ . Besides, the addition of  $\text{LiClO}_4$  into GPEs polymer matrix causes a shift in urethane, ether, and carbonyl functional groups. The 3D GPEs were thermally stable until it reached a temperature of around 300 °C.

As 10 wt.% sample was determined to have the best performance, the formulation was used to fabricate 3D structure GPEs to test its printability which is the most important characteristic for 3D printing. The formulation was successfully printed into three different designs; honeycomb, interdigitated, and scaffold structures which indicates that the integration of 3D printing into GPEs fabrication was successful. The ability to construct 3D structures of electrolytes is important as it can significantly improve battery performance by providing a larger contact area with electrodes.

## امللخص

ولتلبية الطلب على البطاريات المدجة وعالية الأداء للإلكترونيات المحمولة، يمكن الاستفادة من الطباعة ثلاثية الأبعاد لتعزيز أداء إلكترونيات البوليمر. يوفر هذا العمل طريقة تصنيع جديدة للإلكترونيات البوليمر الهلامية في عملية التصنيع مع (SLA) من خلال دمج الطباعة ثلاثية الأبعاد للطباعة الحجرية المجسمة (GPEs) عن طريق إذابة تركيزات مختلفة من بيركلورات الليثيوم GPEs تم تصنيع GPEs الحفاظ على أداء وثنائي ميثيل فورماميد (PUA) في محلول أكريليت البولي يورثين (%بالوزن 0-25) ( $\text{LiClO}_4$ ) أداء GPEs على  $\text{LiClO}_4$  ثم دراسة تأثير SLA وطباعتها باستخدام طريقة (DMF).

من خلال التحليل الطيفي للمقاومة GPEs تم تمييز الخصائص الكهربائية والمورفولوجية والحرارية ل وتحليل حيود الأشعة السينية (FTIR) ونحويل فورييه للأشعة تحت الحمراء (EIS) الكهروكيميائية و (DSC) وقياس السعرات الحرارية للمسح التفاضلي (TGA) وتحليل قياس الوزن الحراري (XRD) المطبوعة ثلاثية الأبعاد موصلية أيونية عالية عند 1.24 GPEs أظهرت (SEM) المجهر الإلكتروني الماسح منخفض (10% بالوزن). وكانت النتيجة متوافقة مع عدد  $\text{LiClO}_4$  عند تركيز  $10^{-3} \text{ S cm}^{-1}$  على التوالي XRD و *FTIR deconvolution* الأيونات الحرة والجزء غير المتبلور المحدد بواسطة  $\text{LiClO}_4$  علاوة على ذلك، تؤدي إضافة  $\text{LiClO}_4$  حيث أظهر كلاهما أعلى قيمة عند 10% بالوزن إلى حدوث تحول في المجموعات الوظيفية لليورثان والإيثر والكربونيل. كانت GPEs إلى مصفوفة البوليمر ثلاثية الأبعاد مستقرة حرارياً حتى وصلت إلى درجة حرارة حوالي 300 درجة مئوية GPEs.

نظرًا لأنه تم تحديد عينة بنسبة 10% بالوزن للحصول على أفضل أداء، فقد تم استخدام التركيبة لتصنيع نماذج ثلاثية الأبعاد لاختبار قابليتها للطباعة والتي تعد أهم خاصية للطباعة ثلاثية الأبعاد. تمت طباعة GPEs الصيغة بنجاح في ثلاثة تصاميم مختلفة؛ هياكل قرص العسل والمتداخلة والسقالات مما يشير إلى أن دمج كان ناجحًا. تعد القدرة على بناء هياكل ثلاثية الأبعاد من GPEs الطباعة ثلاثية الأبعاد في تصنيع الإلكترونيات أمرًا مهمًا لأنها يمكن أن تحسن أداء البطارية بشكل كبير من خلال توفير مساحة اتصال أكبر مع الأقطاب الكهربائية.

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## LIST OF SYMBOLS AND ABBREVIATIONS

|      |                                   |
|------|-----------------------------------|
| 3D   | Three dimensional                 |
| GPEs | Gel polymer electrolytes          |
| AM   | Additive manufacturing            |
| DMF  | Dimethylformamide                 |
| EIS  | Electrical impedance spectroscopy |
| FTIR | Fourier transform infrared        |
| SEM  | Scanning electron microscopy      |
| XRD  | X-ray powder diffraction          |
| DSC  | Differential scanning calorimetry |
| PUA  | Polyurethane acrylate             |
| S/cm | Siemen per centimeter             |
| TNM  | Transference number               |
| FWHM | Full width at half maximum        |