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POLYMER ELECTROLYTES BASED ON POLY(METYHYL METHACRYLATE) (PMMA): CHARACTERIZATION FOR APPLICATION IN LITHIUM POLYMER BATTERY

AB MALIK MARWAN BIN ALI

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I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This topic has not been submitted to any academic institution or non-academic institution for any other degree of qualification.

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Name of Candidate	Ab Malik Marwan bin Ali
Candidate's ID No.	2003306431
Programme	AS990
Faculty	Faculty of Applied Sciences
Thesis Title	Polymer Electrolytes Based on Poly (Metyhyl Methacrylate) (PMMA): Characterization for Application in Lithium Polymer Battery

Signature of Candidate _____

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ABSTRACT

In the present study, poly(meythyl methacrylate) (PMMA), 30% PMMA-grafted-natural rubber (MG30), lithium triflouromethanesulfonate ($LiCF_3SO_3$ or LiTf), propylene carbonate (PC) and ethylene carbonate (EC) were used in the preparation of solid polymer electrolytes (SPE) and gel polymer electrolytes (GPE). All samples were prepared by solution cast technique. SPE and GPE were characterized by means of physical and electrical spectroscopy in order to find the suitable polymer electrolytes composition for fabrication in lithium polymer cell. The conductivity of all samples was calculated using the bulk resistance value obtained from the complex impedance plot in the frequency range 100 Hz to 1 MHz. The SPE film containing 35 wt.% LiTf in PMMA:LiTf and MG30:LiTf exhibit the highest conductivity of 5.80×10^{-5} S cm^{-1} and 8.39×10^{-4} S cm^{-1}, respectively, at room temperature. A further enhancement in the conductivity was obtained on plasticization to form the GPE. The highest room temperature conductivities of 7.16×10^{-4}, 1.20×10^{-3}, 6.38×10^{-3} and 8.95×10^{-3} S cm^{-1} were achieved with free standing GPE films with composition of 15:9:76 wt.% for PMMA:LiTf:PC, PMMA:LiTf:EC, MG30:LiTf:PC and MG30:LiTf:EC systems respectively. The increase in conductivity observed in the GPE is due to the increase in the number of mobile ions that is associated with conformational free volume and the flexibility of the polymer host upon introduction of plasticizer. Attenuated total reflectance-Fourier transformed infrared (ATR-FTIR) spectroscopy justified that the plasticizer penetrated into the polymer chains and created more free volume by reducing the polymer chain transient cross-linking without perturbing the complexation that occurred between the polymer host and LiTf. Differential scanning calorimetry (DSC) studies confirmed the reduction in transient chain crosslink by the reduction in the value of the glass transition temperature (T_g) of the GPE. The temperature dependence conductivity shows that the conductivity of SPE and GPE was observed to obey the Arrhenius rule below T_g and followed the Vogel-Tamman-Fulcher (VTF) behavior above T_g. The activation energy (E_a) for the highest conducting samples of PMMA and MG30 based polymer electrolytes and the free standing GPE films with composition of 15:9:76 wt.% was

found to be in the sequence of PMMA:LiTf > PMMA:LiTf:PC > PMMA:LiTf:EC with value of 0.341 > 0.331 > 0.326 eV and MG30:LiTf > MG30:LiTf:PC > MG30:LiTf:EC with value of 0.163 > 0.144 > 0.143 eV, respectively. The modulus formalism studies show that both PMMA and MG30 based polymer electrolytes (SPE and GPE) behave as an ionic conductor with the value of the lithium transference numbers, t_{Li^+} found to be in the range of 0.165 to 0.253 and 0.211 to 0.299. The stability window of SPE was observed around 1.7 V for PMMA:LiTf and 1.9 V for MG30:LiTf whereas the window stability of GPE is around 3.3 V for PMMA:LiTf:PC, 3.7 V for PMMA:LiTf:EC and 4.3 V for both MG30:LiTf:PC and MG30:LiTf:EC versus Li^+/Li. The polymer electrolytes with higher window stability of more than 4.2 V versus Li^+/Li were used as an electrolyte in the fabrication of lithium polymer cell. The fabricated cell consisted of lithium metal anode and $LiCoO_2$ (factory grade) cathode whose working voltage is 4.2 V and GPE. The cell with configuration of Li/MG30:LiTf:EC/$LiCoO_2$ showed better cycling efficiency compared to cell with configuration of Li/MG30:LiTf:PC/$LiCoO_2$ at room temperature.

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