

UNIVERSITI TEKNOLOGI MARA

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

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Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

Faculty of Applied Sciences

July 2008

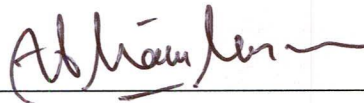
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18 July 2008

ABSTRACT

In the present study, poly(methyl methacrylate) (PMMA), 30% PMMA-grafted-natural rubber (MG30), lithium trifluoromethanesulfonate (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 $5.80 \times 10^{-5} \text{ S cm}^{-1}$ and $8.39 \times 10^{-4} \text{ S cm}^{-1}$, 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 $8.95 \times 10^{-3} \text{ S cm}^{-1}$ 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 LiCoO₂ (factory grade) cathode whose working voltage is 4.2 V and GPE. The cell with configuration of Li/MG30:LiTf:EC/LiCoO₂ showed better cycling efficiency compared to cell with configuration of Li/MG30:LiTf:PC/LiCoO₂ at room temperature.

ACKNOWLEDGEMENT

Firstly, syukur alhamdulillah to Allah Al-mighty. This thesis would not have been written without the help, advice, guidance and information given so willingly by very many people. Their names are endless.

Here, I would like to express my gratitude to my supervisors:

Dr. Muhd Zu Azhan Yahya who always showed me a lot of new ideas.

Associate Professor Dr. Ri Hanum Yahya Subban and Associated Professor Dr. Hadariah Bahron who always provided helpful comments and further insights.

I would also like to express my real appreciation and thanks to the followings for their help with research and technical problems: Misbah, Mat Som, Rozi, Sahak, Yahya, Senah, Aisyah, Cik Yah, Irma, Nurul, Farah, Dr. Razali (SIRIM), Dr. Ahmad Azmin (USM) and not forgetting to Dr. Ali (AMREC SIRIM, Kulim) for assisting me to fabricate the lithium polymer battery.

My sincere gratitude is also conveyed to Universiti Teknologi MARA for the financial support and to MOSTI for the IRPA grant. 09-02-01-0068EA0068.

Finally, I would like to thank to my wife, Sa'adiyah Md Piah for her support and encouragement, my daughters Nur Aisyah, Nur Farhana, Nur Adibah, Nur Fatini and my mother for making this thesis a success.

A.M. M. Ali

July 2008