DEVELOPMENT AND CHARACTERIZATION OF UNPLASTICIZED AND PLASTICIZED CARBOXYMETHYL CELLULOSE DOPED OLEIC ACID SOLID BIO-POLYMER ELECTROLYTES AND ITS APPLICATION IN RECHARGEABLE PROTON BATTERY

CHAI MUI NYUK

SCHOOL OF FUNDAMENTAL SCIENCE
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by
CHAI MUI NYUK

**THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY**

DEDICATION

This thesis is dedicated to

My parents

Late Dad, Chai Kit Sen

Kon Sze Leng

My sisters and brother

Chai Mui Mui

Chai Mui Ai

Chai Mui Xin

Chai Mui Keak

for their endless love and support.

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CHAI MUI NYUK

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In this research, two solid bio-polymer electrolyte (SBE) systems of an unplasticized carboxyl methylcellulose doped with oleic acid (CMC–OA) and a similar system plasticized with Glycerol (CMC–OA–Gly) have been successfully prepared by solution casting technique. Both SBEs system were free-standing, transparent with no phase separation films. Fourier Transform Infrared (FTIR) analysis reveals that complexations have occurred between CMC and OA at 2850 cm^{-1}, 2920 cm^{-1} and 1597 cm^{-1}. No significant complexation was observed with the addition of Gly, hence, Gly has acted as a new pathway which helped in the hopping of H^+ to other coordinating sites of carboxylate anion (COO^-) moiety in CMC. X–Ray Diffraction (XRD) analysis showed the structure of CMC–OA and CMC–OA–Gly as both amorphous. CMC–OA SBE had crystallinity which increased from 9.35 Å to 11.41 Å upon addition of OA till 20 wt. % of OA (OA–20). With the addition of plasticizer (Gly) into CMC–OA SBE, XRD analysis showed that Gly had increased the amorphousness of the SBEs. In electrical impedance

spectroscopy (EIS) analysis, the CMC–OA SBE recorded the highest room temperature conductivity of 2.11 x 10^{-5} S cm^{-1} for sample CMC–OA 20 wt. %. The conductivity increased upon addition of Gly. The CMC–OA–Gly SBE obtained highest conductivity of 1.64 x 10^{-4} S cm^{-1} at room temperature for sample CMC–OA–Gly 40 wt. %. The ionic transport study done via FTIR deconvolution technique showed that the conductivity of CMC–OA is controlled by the ionic mobility and diffusion coefficient, while the conductivity of CMC–OA–Gly is influenced by the number of mobile ions. The mode of ionic conduction in the CMC–OA and CMC–OA–Gly systems were studied by performing transference number measurement (TNM) and was proven that the CMC–OA and CMC–OA–Gly SBEs were proton conductors. Analysis of the frequency exponent showed that the small polaran hopping (SPH) model is the most suitable to explain the hopping mechanism in both CMC–OA and CMC–OA–Gly SBEs. Two coin cell batteries were fabricated using CMC–OA 20 wt. % and CMC–OA–Gly 40 wt. % SBEs. The open circuit voltage (OCV) of Cell 1 that consists of CMC–OA SBE was found to be 0.87 V while for Cell 2 that consists of CMC–OA–Gly SBE was 1.29 V at ambient temperature.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Kedoktoran Falsafah

PENGHASILAN DAN PENCIRIAN KARBOKSIL METILSELULOSA DIDOPKAN ASID OLEIK ELEKTROLIT BIO-POLYMER PEPEJAL TANPA BAHAN PEMPLASTIK DAN BERSAMA BAHAN PEMPLASTIK SERTA APLIKASINYA DI DALAM BATERI PROTON DAPAT DICAS SEMULA

CHAI MUI NYUK

JANUARI 2017

Penyelia Utama : Profesor Madya Mohd Ikmar Nizam Bin Haji Mohamad Isa, PhD

Pusat Pengajian : Pusat Pengajian Sains Asas

Dua sistem elektrolit biopolimer pepejal (SBE) yang mengandungi karboksil metilselulosa didop dengan asid oleik (CMC–OA) dan sistem sama yang ditambahkan gliserol sebagai bahan pemplastik (CMC–OA–Gly) telah dihasilkan melalui teknik penuangan larutan dalam kajian ini. Kedua-dua sistem elektrolit biopolimer pepejal yang diperoleh adalah berbentuk bebas, bersifat lutsinar dan tiada pengasingan fasa. Analisis spektroskopi Inframerah transformasi Fourier (FTIR) telah menunjukkan kompleksasi telah berlaku di antara CMC dan OA pada 2850 cm^{-1}, 2920 cm^{-1} dan 1597 cm^{-1}. Tiada kompleksasi ketara dapat diperhatikan dengan penambahan Gly di mana Gly telah bertindak sebagai laluan baru untuk membantu H^+ melompat ke tapak koordinasi anion karbosilat (COO^-) di CMC. Analisis pembelauan Sinar–X (XRD) menunjukkan struktur CMC–OA dan CMC–OA–Gly SBE adalah amorfus. Saiz kristal CMC-OA SBE meningkat dari 9.35 Å kepada 11.41 Å dengan peningkatan kandungan OA sehingga 20 wt. % OA (OA–20). Analisis XRD menunjukkan keamorfusan SBE meningkat dengan

penambahan bahan pemplastik (Gly) dalam CMC–OA SBE. Di dalam ujian spektroskopi impedans elektrik (EIS), CMC–OA SBE memperoleh kekonduksian suhu bilik tertinggi iaitu 2.11 x 10^{-5} S cm^{-1} bagi sampel CMC–OA 20 wt. %. Kekonduksian telah meningkat selepas Gly ditambahkan. Kekonduksian tertinggi pada suhu bilik ialah 1.64 x 10^{-4} S cm^{-1} untuk sampel CMC–OA 40 wt. %. Kajian pergerakan ionik melalui teknik dekonvolusi FTIR menunjukkan kekonduksian CMC–OA adalah bergantung dengan pekali difusi dan kebolehgerakan ion, malah kekonduksian CMC–OA–Gly pula bergantung pada jumlah ion yang bergerak. Jenis kekonduksian untuk CMC–OA dan CMC–OA–Gly telah dikaji dengan menggunakan teknik pengukuran nombor pemindahan (TNM) dan disahkan CMC–OA dan CMC–OA–Gly SBE merupakan pengalir proton. Analisis eksponen frekuensi telah menunjukkan model lompatan kecil polaran (SPH) adalah paling sesuai untuk menerangkan mekanisma lompatan dalam kedua-dua sistem CMC–OA dan CMC–OA–Gly SBE. Dua bateri berbentuk syiling telah difabrikasi menggunakan CMC–OA 20 wt. % dan CMC–OA–Gly 40 wt. % SBE. Voltan litar terbuka (OCV) untuk Cell 1 yang mengandungi CMC–OA SBE menunjukkan 0.87 V dan Cell 2 yang mengandungi CMC–OA–Gly memperolehi 1.29 V telah dikaji menggunakan RMS multimeter pada suhu bilik.