

**DEVELOPMENT OF CARBOXYMETHYL
CELLULOSE BASED PROTON CONDUCTING
BIOPOLYMER ELECTROLYTES AND ITS
APPLICATION IN SOLID-STATE
PROTON BATTERY**

AHMAD SALIHIN BIN SAMSUDIN

**Thesis Submitted in Fulfillment of the
Requirement for the Degree of Doctor of
Philosophy in the School of Fundamental
Science, Universiti Malaysia Terengganu**

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**Main Supervisor : Associate Professor Dr. Mohd Ikmar Nizam Bin
Hj. Mohamad Isa**

School : School of Fundamental Science

The chronicle in the field of alternative energy for energy storage has shown an excellent progress for the past few years. The increasing interest in green energy storage materials with the development of polymer or biopolymer as electrolytes candidate has attracted great attention. It can offer a number of high-value opportunities, provided that lower costs can be obtained besides environmental friendly. Due to this matter, in this work, two systems, comprising of a biopolymer host, carboxymethyl cellulose doped with ammonium bromide (CMC–NH₄Br) and a similar system plasticization with ethylene carbonate (CMC–NH₄Br–EC) are presented. Both proton conducting biopolymer electrolytes (PCBEs) system were prepared via solution casting technique. The CMC–NH₄Br unplasticized PCBEs exhibit highest room temperature conductivity of about $1.12 \times 10^{-4} \text{ Scm}^{-1}$ for sample containing 25 wt. % NH₄Br. The conductivity was enhanced to $3.31 \times 10^{-3} \text{ Scm}^{-1}$ for the

plasticized sample (CMC–NH₄Br–EC) containing 8 wt. % EC. In the FTIR study, the complexation between CMC and NH₄Br was observed in the wavenumber region between 1600 cm⁻¹ and 1000 cm⁻¹ in both systems. No interaction was found between CMC and EC which shows that EC acted as catalyst which helped the dissociation of H⁺ whilst creating new pathways for H⁺ to hop to other coordinating sites (oxygen) of COO⁻ moiety in CMC. X-ray Diffraction (XRD) analysis showed that the amorphousness of the samples increased with addition NH₄Br which supports the conductivity results. Similar behaviour was also observed for the plasticized sample. The crystallite size reduced with the increase of amorphousness of the system from 12.82 Å to 8.73 Å. From Thermo Gravimetric Analysis (TGA), the thermal stability increased following the conductivity values. Calculation using the Rice and Roth model, activation energy and transference number provides mobility and diffusion coefficient value for the mobile ions, which supports the reported experimental results. The conduction of the ions is proposed to occur by small polaron hopping (SPH) model for CMC–NH₄Br PCBEs system while the plasticized PCBEs system followed quantum mechanical tunnelling (QMT) model. Results from the complex permittivity suggest that the ions have to cross over a potential barrier between sites. Solid–state protonic cell fabricated from the highest conducting sample of CMC–NH₄Br and CMC–NH₄Br–EC PCBEs system produced a maximum open circuit voltage of 1.36 V and 1.48 V respectively at ambient temperature.

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

**PEMBANGUNAN PENGALIR PROTON BIOPOLIMER ELEKTROLIT
BERASASKAN KARBOSIMETIL SELULOSA DAN APLIKASINYA DI
DALAM BATERI PENGALIR PROTON KEADAAN PEPEJAL**

AHMAD SALIHIN BIN SAMSUDIN

JUNE 2014

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Pusat Pengajian : Pusat Pengajian Sains Asas

Kekronikan dalam bidang tenaga alternatif untuk penyimpanan tenaga telah menunjukkan kemajuan yang sangat baik untuk beberapa tahun kebelakangan ini. Kepentingan yang semakin meningkat dalam bahan-bahan penyimpanan tenaga hijau dengan pembangunan polimer atau biopolimer sebagai calon elektrolit telah menarik perhatian yang besar. Ia boleh menawarkan beberapa peluang yang bernilai tinggi, dengan syarat bahawa kos yang lebih rendah boleh diperolehi selain mesra alam. Oleh kerana perkara ini, di dalam kajian ini, dua sistem, yang mengandungi karbosimetil selulosa sebagai biopolimer perumah didopkan dengan ammonium bromida (CMC-NH₄Br) dan sistem yang sama dengan etelina karbonat sebagai bahan pemplastik (CMC-NH₄Br-EC) dibentangkan. Kedua-dua sistem biopolimer elektrolit pengalir proton (PCBE) telah disediakan melalui teknik tebaran larutan. PCBE CMC-NH₄Br tidak terplastikkan memberikan kekonduksian

tertinggi pada suhu bilik sebanyak $1.12 \times 10^{-4} \text{ Scm}^{-1}$ untuk sampel yang mengandungi 25 wt. % NH_4Br . Kekonduksian telah meningkat kepada $3.31 \times 10^{-3} \text{ Scm}^{-1}$ bagi sampel terplastikkan (CMC- NH_4Br -EC) yang mengandungi 8 wt. % EC. Di dalam kajian FTIR, interaksi di antara CMC dan NH_4Br boleh dilihat pada julat nombor gelombang 1600 cm^{-1} sehingga 1000 cm^{-1} di dalam kedua-dua sistem PCBE. Tiada interaksi dikesan di antara CMC dan EC yang menunjukkan bahawa EC bertindak sebagai pemangkin yang membantu penceraian H^+ disamping menghasilkan laluan baru untuk H^+ melompat ke tapak koordinasi lain di dalam (oksigen) moiety CMC. Analisis belauan sinar-x (XRD) menunjukkan keamorfusan sampel-sampel meningkat dengan penambahan NH_4Br yang menyokong keputusan kekonduksian. Sifat yang sama juga dapat diperhatikan untuk sampel terplastikkan. Saiz kristal menurun dengan peningkatan keamorfusan sistem daripada 12.82 \AA ke 8.73 \AA . Daripada analisis gravimetrik terma (TGA), peningkatan kestabilan terma berkadaran dengan nilai kekonduksian. Pengiraan menggunakan model Rice dan Roth, tenaga pengaktifan dan nombor pemindahan memberikan nilai mobiliti dan pengkali resapan untuk ion yang agak sepadan dengan nilai yang diperolehi daripada keputusan eksperimen. Kekonduksian ion dicadangkan telah berlaku melalui model lompatan kecil polaron (SPH) bagi sistem PCBE CMC- NH_4Br manakala bagi sistem PCBE yang terplastikkan mengikuti model penerowongan mekanikal kuantum (QMT). Hasil daripada keputusan permitiviti kompleks menunjukkan bahawa ion-ion perlu melepasi suatu potensi halangan di antara dua tapak penempatan. Sel pengalir proton keadaan pepejal yang difabrikasi daripada sampel sistem PCBE CMC- NH_4Br

dan CMC-NH₄Br-EC menghasilkan voltan litar terbuka maksimum sebanyak 1.36 V dan 1.48 V masing-masing pada suhu bilik.