

**IONIC CONDUCTIVITY AND RELATED STUDIES ON
CHITOSAN-BASED ELECTROLYTES WITH
APPLICATION IN SOLAR CELLS**

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**FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

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CHITOSAN-BASED ELECTROLYTES WITH
APPLICATION IN SOLAR CELLS**

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**THESIS SUBMITTED IN FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY**

**DEPARTMENT OF PHYSICS
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2012

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I hereby declare that the work reported in this thesis is my own unless specified and duly acknowledged by quotation.

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August 2012

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**Ionic conductivity and related studies on chitosan-based electrolytes with
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ABSTRACT

The motivation in this work is to ensure that the chitosan biopolymer can be used as a host for ion conduction and used as an electrolyte in dye-sensitized solar cells (DSSCs). The conductivity of the chitosan-NH₄I electrolytes was optimized by varying the NH₄I concentration, blending chitosan with PVA and PEO and also by incorporating of ionic liquid (IL). The electrolytes were prepared by solution cast technique. FTIR results confirm complexation between polymer, NH₄I and IL. Hydrogen bonding between chitosan and PVA and between chitosan and PEO are observed in the respective spectrum. XRD indicates that the amorphousness of pure chitosan, chitosan-PVA and chitosan-PEO films changes with NH₄I concentration. The 55 wt.% chitosan-45 wt.% NH₄I (Ch9) sample exhibits the highest room temperature conductivity of $3.73 \times 10^{-7} \text{ S cm}^{-1}$. Blending chitosan with PVA and PEO further increased conductivity. The 27.5 wt.% chitosan-27.5 wt.% PVA-45 wt.% NH₄I (CV5) sample exhibits the highest conductivity of $1.77 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature and the highest conducting sample in (chitosan-PEO)-NH₄I system is $3.66 \times 10^{-6} \text{ S cm}^{-1}$ for sample containing 16.5 wt.% chitosan-38.5 wt.% PEO-45 wt.% NH₄I (CEO7) electrolyte. Incorporating 50 wt.% IL into Ch9, the electrolyte CIL5 exhibits the highest room temperature conductivity of $3.43 \times 10^{-5} \text{ S cm}^{-1}$. The activation energy, E_A for the highest conducting samples follows the order Ch9 (0.45 eV) < CV5 (0.38 eV) < CEO7 (0.31 eV) < CIL5 (0.25 eV). DSSCs were fabricated using natural dyes extracted from black rice, blueberry and red cabbage. The highest conducting samples from each system have been chosen in the fabrication DSSCs. Some iodine crystals were added to the electrolytes to produce the redox-mediator. Red cabbage DSSCs using CIL5(+I₂) gel electrolyte exhibits the highest efficiency of 0.2 % compared to using CEO7(+I₂) and CV5(+I₂) gel electrolytes.

ABSTRAK

Objektif utama kajian ini adalah untuk memastikan bahawa biopolimer chitosan boleh digunakan sebagai perumah untuk mengkonduksi ion dan digunakan sebagai elektrolit di dalam “dye-sensitized solar cells” (DSSCs). Kekonduksian chitosan-NH₄I elektrolit telah dioptimumkan dengan mengubah kepekatan NH₄I, mencampurkan chitosan dengan PVA dan PEO dan dengan cecair ionik. Teknik penuangan di dalam piring Petri digunakan dalam penyediaan elektrolit. FTIR mengesahkan bahawa berlakunya interaksi diantara polimer dengan NH₄I dan cecair ionik. Ikatan hidrogen di antara chitosan dengan PVA dan chitosan dengan PEO dapat dilihat dalam spektrum FTIR. XRD menunjukkan sifat amorphous di dalam chitosan tulen, chitosan-PVA dan chitosan-PEO berubah dengan kepekatan NH₄I. Sample berkomposisi 55% chitosan-45% NH₄I (Ch9) menunjukkan kekonduksian tertinggi pada suhu bilik sebanyak $3.73 \times 10^{-7} \text{ S cm}^{-1}$. Kekonduksian elektrolit meningkat dengan mencampurkan chitosan dengan PVA dan PEO. Sampel berkomposisi 27.5% chitosan-27.5% PVA-45% NH₄I (CV5) menunjukkan kekonduksian tertinggi pada suhu bilik sebanyak $1.77 \times 10^{-7} \text{ S cm}^{-1}$ dan $3.66 \times 10^{-6} \text{ S cm}^{-1}$ untuk sampel berkomposisi 16.5% chitosan-38.5% PEO-45% NH₄I (CEO7). CIL5 elektrolit memberikan kekonduksian tertinggi pada suhu bilik sebanyak $3.43 \times 10^{-5} \text{ S cm}^{-1}$ apabila 50% cecair ionik dimasukkan ke dalam Ch9. Tenaga pengaktifan, E_A tertinggi bagi setiap sistem adalah mengikut aturan Ch9 (0.45 eV) < CV5 (0.38 eV) < CEO7 (0.31 eV) < CIL5 (0.25 eV). Pewarna semula jadi yang diekstrak daripada pulut hitam, kubis merah dan blueberry digunakan dalam pemfabrikatan DSSCs. Iodin ditambah kepada elektrolit bagi menghasilkan pengantara redoks. DSSCs kubis merah yang menggunakan CIL5(+I₂) elektrolit gel mempamerkan kecekapan tertinggi sebanyak 0.2% berbanding dengan CEO7(+I₂) dan CV5(+I₂) elektrolit gel.

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ABBREVIATIONS

(NCS) ₂	Diisothiocyanate	DEC	Diethylene carbonate
NaI	Sodium iodide	NaBiF ₄	Bismuth sodium fluoride
KI	Potassium iodide	LiClO ₄	Lithium perchlorate
I ₂	Iodine	MC	Methyl cellulose
LiI	Lithium iodide	PVAc	Polyvinyl acetate
Pr ₄ NI	Tetrapropylammonium iodide	PMMA	Poly(methyl methacrylate)
AgNO ₃	Silver nitrate	PA	Palmitic acid
TBP	4-tert-butyl pyridine	OA	Oleic acid
PC	propylene carbonate	J_{sc}	Short-circuit current density
LiCF ₃ SO ₃	Lithium triflate	V_{oc}	Open-circuit voltage
EC	Ethylene carbonate	ff	Fill factor
NaClO ₄	Sodium perchlorate	η	Efficiency (%)
LiOAc	Lithium acetate		
NH ₄ NO ₃	Ammonium nitrate		
PEG	Poly(ethylene glycol)		
LiNO ₃	Lithium nitrate		
H ₂ SO ₄	Sulfuric acid		
NMP	N-methyl pyrrolidone		
KOH	Potassium hydroxide		
ZnCF ₃ SO ₃	Zinc triflate		
DOP	dioctyl phthalate		
H ₃ PO ₄	Phosphoric acid		
DMPImI	1-propyl-2,3 dimethylimidazolium iodide		
LiCAC	lithium complexed acetylated chitosan		

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