

ENHANCEMENT OF IONIC CONDUCTIVITY IN POLYACRYLAMIDE BASED  
POLYMER ELECTROLYTES FOR TIN-AIR BATTERIES

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## ABSTRACT

The purpose of this research is to study the ionic conductivities of gel polymer electrolytes (GPEs) and composite solid polymer electrolytes (CSPEs) for tin-air battery application based on polyacrylamide as host polymer. Methanesulfonic acid and p-toluenesulfonic acid were used as additives. Electrochemical impedance spectroscopy (EIS) was used to measure the ionic conductivities of the samples by using the bulk electrolyte resistance values ( $R_b$ ). The FTIR spectra were analyzed to describe the mechanism involved in the proton transfer within the membranes by referring to the characteristic shifts of the absorbance bands of C=O and N-H<sub>2</sub>. Tin-air batteries, with a configuration of Sn(anode)/GPE/ air(cathode) were fabricated to study the electrochemical properties of the GPEs. The batteries were discharged at various constant of current densities. The results showed that the maximum ionic conductivities of  $7.0 \times 10^{-1}$  S/cm and  $9.34 \times 10^{-1}$  S/cm were obtained for GPEs at a loading of 3.0 M MSA and 5.0 M of pTSA respectively. The highest ionic conductivity of  $1.17 \times 10^{-6}$  S/cm and  $4.45 \times 10^{-5}$  S/cm were observed at 5.0 M and 4.0 M loading of MSA and pTSA into CSPEs. The FTIR spectra indicated that the proton transfer in GPEs occurred through the protonation of NH<sub>2</sub> group of PAAM. Whereas, in CSPEs the protons were transferred from sulfonic acid to the functional group of C=O of PAAM through the formation of hydrogen bond. The OCV exhibited by tin-air cell of PAAM-MSA GPE was 1.27 V compared to 1.23 V for cell with PAAM-pTSA GPE. The tin anode of the cell for PAAM-MSA GPEs produced an average specific discharge capacity of 456mAh/g, while for PAAM-pTSA GPEs was 439 mAh/g. The tin-air cell of PAAM-MSA GPEs also supported a relatively high current of 12 mA/cm<sup>2</sup> with a maximum power density of 5.25 mW/cm<sup>2</sup>. In conclusion, the research showed that MSA and pTSA as additives enhanced the ionic conductivity of the PAAM electrolytes. The mechanism involved in the proton transfer of GPEs is different from the mechanism in CSPEs. The tin-air battery cell with PAAM-MSA GPE exhibited superior electrochemical cell performance in the discharge capacity. Thus, this research proves that PAA-MSA GPEs have high potential for application as tin-air battery.



## PENINGKATAN KEKONDUKSIAN IONIK POLIMER POLIAKRILAMIDA ELEKTROLIT DALAM PENYEDIAAN BATERI TIN-UDARA

### ABSTRAK

Tujuan kajian ini adalah mengkaji kekonduksian ionik bagi polimer electrolit bergel (GPEs) dan polimer electrolit pepejal berkomposit (CSPEs) untuk diaplikasikan dalam bateri tin-udara. Polimer poliakrilamida (PAAm) digunakan sebagai perumah. Asid metanasulfonik (MSA) dan asid para-toluenasulfonik monohidrat (pTSA) digunakan sebagai bahan tambah dalam elektrolit. Kaedah EIS digunakan untuk mengkaji konduksian ionik bagi semua sampel daripada nilai rintangan pukal ( $R_b$ ). Mekanisma pergerakan proton dalam polimer elektrolit yang disintesis, dijelaskan dengan menggunakan jalur C=O dan NH<sub>2</sub> pada spectra FTIR. Bateri tin-udara berkonfigurasi Sn(anod)/GPE/udara(katod) dibentuk untuk mengkaji ciri-ciri elektrokimia GPEs yang disintesis. Kesemua bateri dinyahcaskan dengan menggunakan aliran elektrik berbeza. Dapatan kajian menunjukkan konduksian maksimum yang bernilai  $7.0 \times 10^{-1}$  S/cm dan  $9.34 \times 10^{-1}$  S/cm telah diperolehi dengan penambahan 3.0 M MSA dan 5.0 M pTSA secara berasingan dalam GPEs. Bagi CSPEs, konduksian ionik optimum yang bernilai  $1.17 \times 10^{-6}$  S/cm dan  $4.45 \times 10^{-5}$  S/cm diperolehi dengan penambahan 5.0 M MSA dan 4.0 M pTSA ke dalam polimer matriks masing-masing. Analisis spektra FTIR menunjukkan bahawa mobiliti proton dalam GPEs berlaku melalui mekanisme protonasi kumpulan berfungsi NH<sub>2</sub> dalam polimer. Manakala, mobiliti proton dalam CSPEs berlaku melalui.. pembentukan ikatan hidrogen di antara asid sulfonik dengan kumpulan berfungsi C=O pada polimer. Anod Sn bagi bateri dengan PAAm-MSA GPE telah menghasilkan purata kapasiti discas spesifik (456mAh/g) dan nilai OCV (1.27V) yang lebih tinggi berbanding dengan PAAm-pTSA. Purata kapasiti spesifik bagi anod Sn dengan PAAm-pTSA GPE adalah 439 mAh/g dengan nilai OCV 1.23 V. Bateri tin-udara dengan PAAm-MSA sebagai elektrolit juga boleh mengendalikan arus elektrik setinggi 12 mA/cm<sup>2</sup> dengan ketumpatan kuasa 5.25 mW/cm<sup>2</sup>. Kesimpulannya, penambahan asid sulfonik ke dalam matriks polimer telah meningkatkan konduksian ionik dalam PAAm-MSA GPEs dan PAAm-pTSA GPEs. Mekanisme mobiliti proton dalam GPEs adalah berbeza berbanding dengan mobiliti proton dalam CSPEs. PAAm-MSA GPEs menunjukkan ciri-ciri elektrokimia yang lebih baik berbanding dengan PAAm-pTSA GPEs. Kajian ini telah membuktikan bahawa PAA-MSA GPEs mempunyai potensi yang tinggi untuk aplikasi bateri tin-udara.



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## LIST OF ABBREVIATIONS

CSPE Composite Solid Polymer Electrolyte

DEC Diethyl Carbonate

DMC Dimethyl Carbonate

DMAc Dimethylacetamide

DMSO Dimethyl Sulphoxide

DSC Differential Scanning Calorimetry

EC Ethylene Carbonate

EIS Electrical Impedance Spectroscopy

FESEM Field Emission Scanning Electron Microscope

FRA Frequency Response Analyser

FTIR Fourier Transform Infrared

GPE Gel Polymer Electrolyte

KHCO<sub>3</sub> Potassium Hydrogen Carbonate

MSA Methanesulfonic Acid

NMP N- methylpyrrolidone

OCV Open Circuit Voltage

PAAm	Polyacrylamide
PAN	Poly(acrylonitrile)
PC	Propylene Carbonate
PEO	Poly(ethylene oxide)
PMMA	Poly(methyl methacrylate)
pTSA	p-Toluenesulfonic acid
PVC	Poly(vinylchloride)
PVdF	Poly(vinylidene fluoride)
R <sub>b</sub>	Bulk Resistance
SPE	Solid Polymer Electrolyte
T <sub>g</sub>	Glass Transition Temperature
TGA	Thermal Gravimetric Analysis
XRD	X-ray Diffraction Analysis



## CHAPTER 1

### INTRODUCTION

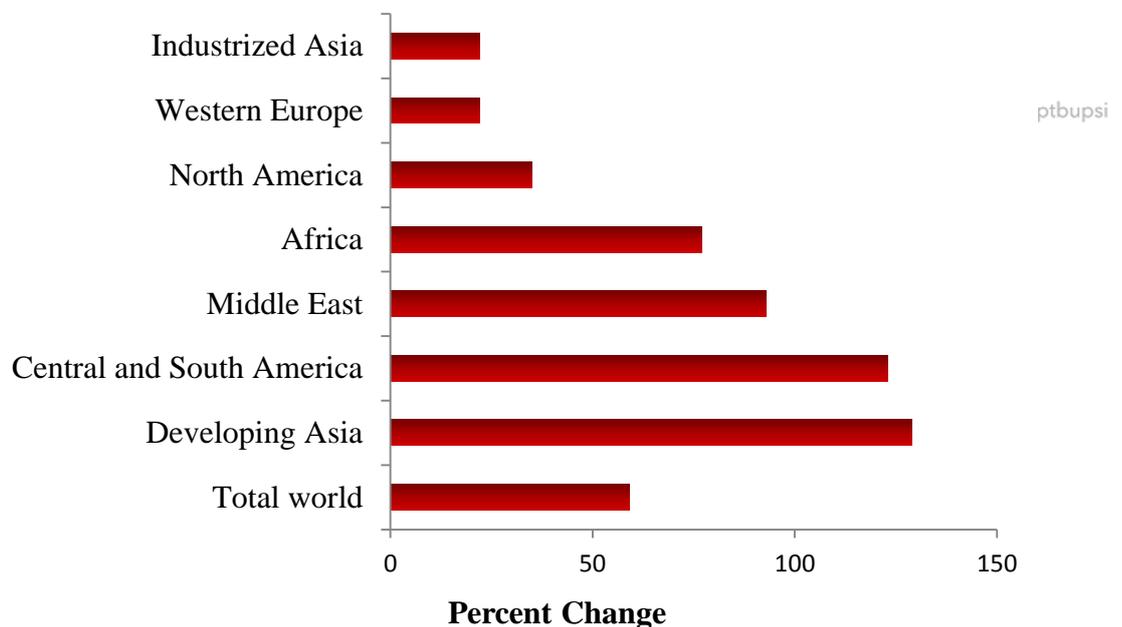


#### 1.1 Introduction

The United Nations Department of Economic and Social Affairs have projected that the world population could eventually reach 10.6 billion, mostly due to the advent and progress of the industrial revolution. Population growth is incumbent on increased energy demands from individuals and societies. The oil and gas prices can be expected to increase dramatically as the demand for energy and power are increasing day by day. This could inevitably result in a future energy crisis. Figure 1.1 shows the projected change in energy demand by region for 30 years, as reported by the U.S Energy information Administration (EIA) in 1999.



There are many global initiatives working towards resolving the energy crisis, mostly in the form of funding research on the exploitation of electrochemical power sources. Examples of these include primary (single use) and secondary (rechargeable) batteries, fuel cells, super-capacitors, and photovoltaic devices. The success of these commercial products is dependent on its viability and reliability. Factors that govern performances include energy density, especially high rate discharges at low temperatures, and performance stability in the context of storage, overcharging, and cycle life. Figure 1.2 depicts human energy needs and ways of meeting them.



*Figure 1.1.* Projected Change in Energy Demand by Region, 1999-2020  
Energy Information Administration, Independent Statistics and Analysis, 1999,  
Retrieved from <http://www.eia.gov/>

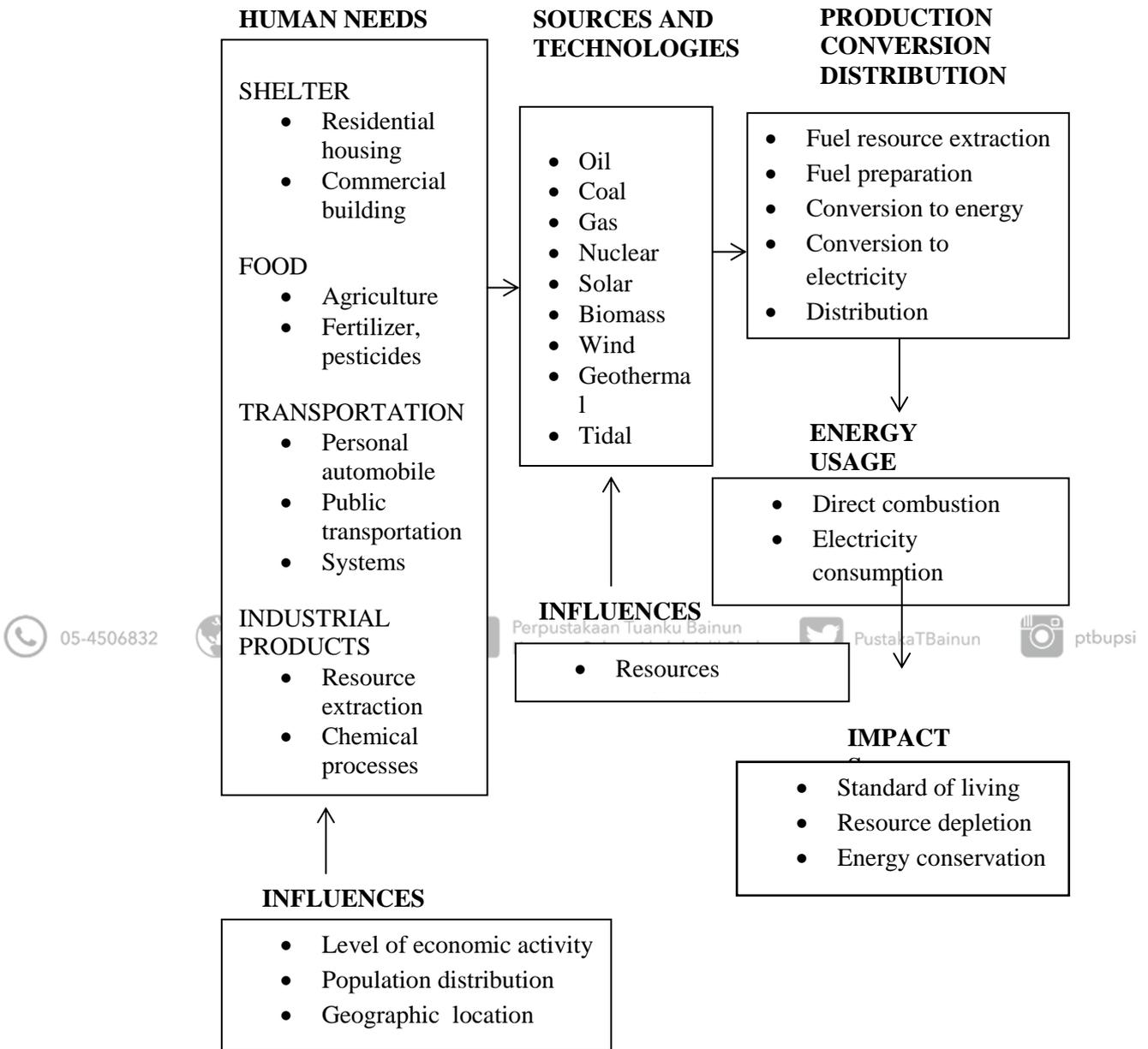


Figure 1.2. Flowcharts of Energy needs by Energy Information Administration, Independent Statistics and Analysis, 1999. Retrieved from <http://www.eia.gov/>

Battery is an essential energy storage device playing a significant role in fulfilling energy demands. It is a transducer that transforms chemical to electrical

energy, which can in turn be utilized by an external device. It is also known as a galvanic cell, as the electrochemical reactions taking place within the batteries are galvanic reactions. Regardless of the form or technology, the basic building block for any kind of battery is referred to as a cell. A battery can be comprised of a single cell, such as the power source used in the common flashlight, to a package of multiple cells wired together in a laptop computer or a device in an automobile (Lee, 2013).

Every battery consists of two electrodes (an anode and a cathode), an electrolyte, and a separator between its anode and cathode. The anode in the battery deserves an equal say in the overall performance of a battery. The negative electrode is associated with the oxidation or release of electrons into the external circuit during electrochemical reactions. The choice of the anode material is essential towards the effective development of a high energy density battery. Several potential solutions for a suitable anode were reported by Winter & Brodd (2004). Anode that is easily handled, efficient reducing agent, excellent conducting agent, good mechanical stability, and low cost is generally preferred.

The cathode is the positive electrode that accepts electrons from the external circuit during electrochemical reactions. Excellent electrical conductor, the retention of structure despite discharges or over charges, low cost, and environmentally benign materials are some of the key requirements for a cathode material in a battery. Almost all research and commercialization of cathode materials are centered on two classes of materials (Rao, 2014). The first type material contains layered compounds with an