DEVELOPMENT OF SCREEN-PRINTED NICKEL-ZINC AND SILVER-ZINC BATTERIES

BY

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ABSTRACT

The current trend for electronics demands portable, miniature, connected, and highly integrated devices, for example, wearable electronics and the internet of things (IoT). Miniaturization of these devices includes shrinking power sources or batteries. Compared to conventional batteries, printed batteries have relatively small form factors and are very thin. The printed battery is a battery system in which most of its components are printable. The batteries' elements, such as electrodes and ionic solutions, are developed in ink form such that it can be printed. For this work, a printed zinc battery was designed, fabricated using a screen printing method, and packaged in a pouch. The zinc battery system is chosen over lithium-ion batteries because of the abundance of zinc; zinc batteries are also cheaper, safe, and environmentally friendly. Screen printing was the fabrication method of choice as it is a widely used method, simple, and relatively cost-effective for research and development. In this research, two different battery systems were developed, compare both performances, which are Ni-Zn and Ag-Zn. Each of the battery elements (current collector, electrodes, electrolytes) were tested separately to evaluate its functionality and performance using electrochemical analyses such as cyclic voltammetry and charge-discharge. Through the experimental studies, polyvinyl butyral was selected as the binder of the battery electrodes due to its better electrochemical performance as compared to polyvinyl pyrrolidone, which is one of the crucial breakthroughs in this project. The selection of silver ink as the current collector was preferred since carbon ink has high resistance, which fails the battery. However, the silver ink is not suitable for cathode current collector, especially for the Ni-Zn system because it reacts on behalf of $Ni(OH)_2$ due to its high reduction potential. Thus, the battery will function as an Ag-Zn battery instead, although the XRD data showed the presence of both Ni(OH)2 and ZnO on cathode and anode, respectively. The printed zinc-silver battery system was tested and was proven to work with a nominal voltage of 1.56V and a discharge capacity of 1.3407 mAh. The electrode surface area was found to be 8.78 $cm^{2,}$ which is equivalent to the areal capacity of 0.153 $mAh.cm^{-2}$ with an overall thickness of 200-250 µm. This work is a proof-of-concept that zinc-silver batteries can be fabricated using screen printing techniques.

خلاصة البحث

يتطلب المسار الحالي في مجال الإلكترونيات أجهزة محمُولة ، مُصغرة ، مُتصلة ومُتكاملة إلى حد كبير مِثل الإلكترونيات القابلة للارتداء وإنترنت الأشياء. تتضمَّن عملية تصغير هذه الأجهزة تقليص مصادر الطاقة أو بطارياتها. عِند مقارنة البطاريات المطبوعة بالبطاريات التقليدية، نجد أن تلك المطبوعة تتميز بعوامل شكلية صغيرة نسبيًا كما أنها رقيقة جدًا. تُعتبر البطارية المطبوعة نظامًا يمكن فيه طباعة معظم مكوِّنات البطارية. يتم صُنع عناصر البطاريات مثل الأقطاب الكهربائية والمحاليل الأيونية على هيئة حبر بحيث يمكن طباعتها فيما بعد. ولهذه الدراسة، تم صناعة بطارية الزنك المطبوعة باستخدام طريقة طباعة الشاشة الحريرية، وتعبئتها في حقيبة. تم اختيار نظام بطارية الزنك بدلًا من بطاريات أيون الليثيوم وذلك لسبب وفرة الزنك. علاوةً على ذلك، فإنَّ بطاريات الزنك أرخص سعرًا كما أنها آمنة وملائمة للبيئة. تُعد طباعة الشاشة الحريرية طريقة التصنيع المختارة لانتشار استخدامها على نطاق واسع ولبساطتها وفعاليَّتها من حيث التكلفة للبحث والتطوير. في هذه الدراسة، تم إنشاء نظامين مختلفين للبطاريات، بطارية Ni–Zn و Ag–Zn ، وتمت مقارنة أداؤهما ببعضهما البعض. كما أنه تم اختبار كل عُنصر من عناصر البطارية (مُجمِّع التيَّار ، الأقطاب الكهربائية و الشوارد الكهربائية) بشكل مُنفصل لتقييم وظائفها وأدائها باستخدام التحليلات الكهروكيميائية مثل قياس الجهد الدوري والتفريغ الكهربائي للشحنة. من خلال التجربة، تم اختيار بولي فينيل بوتيرال كموثق لأقطاب البطارية بسبب أدائه الكهروكيميائي الأفضل بالمقارنة مع البولي فينيل بيروليدون ، وهو أحد الإنجازات الحاسمة في هذا المشروع. تم اختيار الحبر الفضي ليعمل كمجمع التيار بدلًا من الحبر الكربوني لأن الثاني يتمتع بمقاومة عالية ، مما يتسبب في فشل البطارية. ومع ذلك ، فإن الحبر الفضي غير مناسب لمجمع تيار الكاثود ، خاصة بالنسبة لنظام Ni–Zn لأنه يتفاعل نيابة عن Ni(OH)2 بسبب إمكانيته العالية على الخفض. وبالتالي ، ستعمل البطارية كبطارية Ag–Zn بالنيابه عنه، على الرغم من أن بيانات الأشعة السينية XRD أظهرت وجود كل من $Ni(OH)_2$ و ZnO على الكاثود والأنود ، على التوالي. تم اختبار نظام بطارية الزِنك والفَضة المطبوعة وثبت أنه يعمل بجُهد إسمي يبلغ 1.56 فولت وقدرة تفريغ تبلغ 1.3407 مللي أمبير في الساعة. تم العثور على مساحة سطح القطب 8.78 سم^2 والتي تساوي سعة كلية تبلغ 0.153 ميللي امبر/سم $^{-2}$، و نسبة سماكة إجمالية تبلغ 200– 250 µm. هذا البحث هو دليل إثبات على أن بطاريات الزنك والفضة يمكن تصنيعها باستخدام تقنيات طباعة الشاشة الحريرية.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Electronics Engineering)

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Dean, Kulliyyah of Engineering

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Muhamad Aiman Bin Nazri

Signature ………………………………………… Date 18/08/2020…………………...

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LIST OF ABBREVIATIONS

GPS	Global Positioning System
NFC	Near-field communication
Wi-FI	Wireless fidelity
IoT	Internet of things
RFID	Radio-frequency identification
LED	Light emitting diode
EMV	Europay, MasterCard, and Visa
Redox	Reduction-oxidation
NiOOH	Nickel oxyhydroxide
$Ni(OH)_2$	Nickel (II) hydroxide
Zn	Zinc
ZnO	Zinc oxide
$Zn(OH_4)^{2-}$	Zincate ion
OH^-	Hydroxyl ion
H_2O	water
OCV	Open circuit voltage
Ag	Silver
Ag_2O	Silver oxide
TPU	Thermoplastic polyurethane
KOH	Potassium hydroxide

AM	Active materials
HER	Hydrogen evolution reaction
$Ca(OH)_2$	Calcium hydroxide
In_2O_3	Indium (III) oxide
Ga_2O_3	Galium (III) oxide
$In(OH)_3$	Indium (III) hydroxide
CdO	Cadmium oxide
PbO	Lead oxide
Ti_2O_3	Titanium (III) oxide
Hg	Mercury
HgO	Mercury oxide
MnO_2	Manganese dioxide
MWCNTs	Multiwalled -carbon nanotubes
PAC	Polyvinyl alcohol cellulose
FPC	Flexible printed circuit
IPA	Isopropyl alcohol
CV	Cyclic voltammetry
Al_2O_3	Aluminum oxide
TiO_2	Titanium dioxide
Bi_2O_3	Bismuth (III) oxide
K_2CO_3	Potassium carbonate
KF	Potassium fluoride
NiO	Nickel (II) oxide

PC	Polycarbonate
PTFE	Teflon (polytetrafluoroethylene)
PVB	Polyvinyl butyral
PVP	Polyvinyl pyrrolidone
PVDF	Polyvinylidene fluoride
NMP	N-methyl-2-pyrrolidone
SBR	Styrene butadiene rubber
PEO	Polyethylene oxide
AB	Acetylene black
BMIM	1-butyl-3-methylimidazolium trifluoromethanesulfonate
HFP	Hexafluoropropene
CMC	Carboxymethyl cellulose
PSBR	Modified styrene butadiene rubber
PSSNa	Poly (styrene sulfonate sodium)
PEDOT:PSS	Poly (3,4-ethylenedioxythiophen) : poly (styrene sulfonate)
PEI	Polyethyleneimine
SIS	Poly-styrene-block-polyisoprene-block-polystyrene
SP	Super P conductive carbon black
PP	Polypropylene
PE	Polyethylene
GDL	Gas diffusion layer
DC	Direct current
PET	Polyethylene Terephthalate

WE	Working electrode
RE	Reference Electrode
CE	Counter Electrode
S	Sense
AgCl	Silver chloride
NaOH	Sodium hydroxide
SHE	Standard hydrogen electrode
C	Carbon
BET	Brunauer-Emmett-Teller (surface area analysis)
SEM	Scanning Electron Microscope
XRD	X-ray Diffraction

LIST OF SYMBOLS

Wh/kg	Specific energy density
Wh/L	Volumetric energy density
V	Voltage
d	Diameter
w	Mesh opening
wt%	Weight percentage
A	Current
s	Second
mAh	Capacity
Pa	Yield Stress
$mAh.cm^{-2}$	Areal capacity
$mA.cm^{-2}$	Current density
h	Hour
mAh/g	Specific capacity
Ω/sq	Sheet resistance
cP	Viscosity
rpm	Rotational speed
°C	Degree celcius
mV/s	Potential scan rate
M	Molarity

g	gram
m_2/g	Specific surface area
E^o	Standard cell potential
ē	Electron
	Rate at which a battery is discharged relative to its maximum
C	Capacity

CHAPTER ONE

INTRODUCTION

1.1 OVERVIEW

Nowadays, due to the advancement of technology, electronic devices are getting smaller and smaller over time, and many features can be integrated into a single device like smartphones that have cameras, GPS, music player, video player, Bluetooth, NFC, Wi-Fi, etc. Due to the multiple features built-in, users will bring along the device wherever they go in daily life. So, the portability of the device is really important since it will provide a better user experience. In the future, the market trend is aiming for wearable devices, Internet of Things (IoT), and environmental sensors (He, 2015). With this trend envisioned, industries are aiming further to shrink the current electronic devices at the same time introduce new technology whereby our daily things such as outfits, shoes, watch, and wallet can become intelligent by integrating them with electronics, sensors, actuators, display and most importantly energy supply which is the battery. Therefore, the battery must be small and thin form factor to fit in into those devices, unlike the conventional batteries, whereby there are thick and bulky, which cannot fit into small form factor electronic devices.

Lithium-ion batteries are the most well-known battery used in most of the electronic devices today, such as laptops, smartphones, cameras, smartwatches, etc. because of high energy density and high life cycle. However, it is expensive, not environmentally friendly, flammable, and very strict handling conditions due to its moisture sensitivity. So, zinc batteries are preferred because of abundance, cheap, environmentally friendly, and room temperature handling. The development of printed zinc batteries is a cost-effective way to research and explore more on printed battery technologies.

1.2 PROBLEMS STATEMENT AND ITS SIGNIFICANCE

Most of the consumer product industries are towards miniaturization of electronic devices, whereby they become more portable, compact, and convenient to be worn all the time. However, with the currently available technology, there are still a lot of constraints to minimize the size of the devices. One of the reasons is the size of the battery that needs to be used to supply electricity to the device. This problem is caused by the bulky design of the conventional battery, which prevents the battery from fitting into the small form factor device. For example, the next generation of a smart card is going towards powered smart cards in which the conventional EMV card is featured with an additional built-in battery, microcontroller unit, and other features such as NFC, RFID, acoustics, LED lights, and fingerprint sensor (Davies, 2018). This project is very significant as it is estimated that the market for flexible batteries to be worth USD 471 million in the year 2026 (He, 2015).

A lot of researches have been done related to printed zinc batteries. One of the problems that were addressed is the low open-circuit voltage of the zinc battery. Besides that, with the reduction of the size of the battery, will compromise its capacity. Another problem with zinc-based battery with its low of the charge-discharge cycle due to corrosion of zinc and dendritic growth of zinc (Banik & Akolkar, 2015; Pei, Wang, & Ma, 2014) which leads to short circuit. Furthermore, issues such as zinc passivation and zinc dissolution also shorten the life cycle of zinc-based batteries. Therefore, to produce such a reliable printed battery, these problems need to be addressed, especially for a rechargeable battery system so that it can be used as an alternative for lithium-ion batteries due to its cheaper cost, environmentally friendly, non-flammable, and safe.

1.3 RESEARCH OBJECTIVES

This project aims to achieve these objectives:

1. To develop a thin, screen-printed nickel-zinc and silver-zinc battery.
2. To test and evaluate the performance of the developed screen-printed zinc battery.
3. To compare the developed screen-printed battery performance with other developed battery.

1.4 RESEARCH METHODOLOGY

The research started with conducting a literature review towards understanding the fundamentals of battery, printing technologies, printed battery, design, etc. Then, a simple printed battery is designed as the test vehicle for the research. Next, fabrication of the printed battery will be kicked off and followed by packaging. Furthermore, every single element of the printed battery, such as current collector, anode, cathode, and electrolyte, are tested and evaluated before the final printed battery testing. Finally, the results will be analyzed and concluded. The flow chart of the research methodology is shown in Figure 1.1 below.

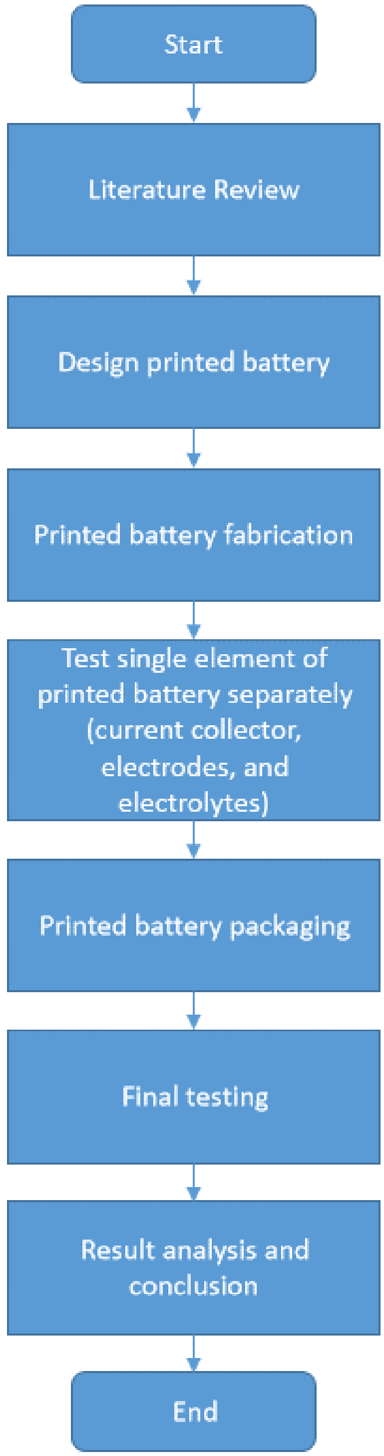

Figure 1. 1 Research Methodology