

# Sudan University of Science and Technology College of graduate Studies



# Electrochemical Performance of Laser Modified Zinc Electrode

الاداء الكهروكيميائي لقطب الخارصين المعدل بالليزر

A Thesis Submitted As Partial Fulfillment of The Requirements For The Degree of Master of Science In Physics.

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February 2017

# الآيه

# قال تعالى:

(لَقَدْ أَرْسَلْنَا رُسُلَنَا بِالْبَيِّنَاتِ وَأَنزَلْنَا مَعَهُمُ الْكِتَابَ وَالْمِيزَانَ لِيَقُومَ النَّاسُ بِالْقِسْطِ فَ وَأَنزَلْنَا الْمَدِيدَ فِيهِ بَأْسٌ شَدِيدٌ وَمَنَافِعُ لِلنَّاسِ وَلِيَعْلَمَ اللَّهُ مَن يَنصُرُهُ وَرُسُلَهُ فِأَنزَلْنَا الْمَدِيدَ فِيهِ بَأْسٌ شَدِيدٌ وَمَنَافِعُ لِلنَّاسِ وَلِيَعْلَمَ اللَّهُ مَن يَنصُرُهُ وَرُسُلَهُ بِالْغَيْبِ وَإِنَّ اللَّهَ قَوِيٌّ عَزِيزٌ)

(سورة الحديد الآية 25)

# **Dedications**

To

My father
My mother
My family
My friends

# **Acknowledgments**

I would like to thanks allah for giving me the strength to finish this study. Special thanks to Dr Ali Abdel Rahman Saeed Marouf, supervisor of my thesis for his guidance and assistance throughout the progress of this thesis. My thanks extend to the staff of institute of laser, and college of science (physics & chemistry) departments for their assistance in the experimental work. Finely thanks to Khartoum University for giving me electrodes materials.

# **Abstract**

In this research  $CO_2$  laser has been utilized to produce textured surface in zinc foil to use in electrochemical cells as cathode, modified surface was obtained by making two parallel lines in 1mm,using  $CO_2$  laser with ( $\Lambda \equiv 10600$ nm) and power of 90 watts and 10mm/s speed. The experimental evidence of the effect of surface texturing on the performance of electrochemical cell was demonstrated and investigated. The results show considerable increase in cell voltage with the textured cathode comported to the planar one, also the performance of cell with textured cathode is more stable.

# المستخلص

في هذا البحث أستخدم ليزر ثاني اكسيد الكربون لانتاج اسطح نسيجيه في الواح الخارصين لاستخدامها اقطاب سالبه في الخلايا الكهروكيميائيه. تم الحصول علي السطح المعدل بعمل خطين متوازيين في الملمتر الواحد باستخدام ليزر ثاني اكسيد الكربون (10600 نانوميتر) بقدرة 90 وات وسرعة 10ملم/ثانيه. الدليل العملي لتاثير السطح النسيجي علي اداء الخليه الكهروكيميائيه تم توضيحه والتحقق منه. اظهرت النتائج زياده مقدره في جهد الخليه ذات القطب السالب النسيجي مقارنه بذلك المسطح وايضا وجد ان اداء الخليه ذات القطب السالب النسيجي اكثر استقرار.

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# **CHAPTER ONE**

# Introduction and Literature Review

#### 1.1 Introduction

The electron-transfer reactions that occur at the surface of a metal immersed in a solution take place near the surface of the electrode, so there is no way that the electrons passing between the solution and the electrode can be channeled through an instrument to measure their voltage or to control the rate of the reaction. If we have two such metal-solution interfaces, we can easily measure a potential difference between them, such an arrangement is called a galvanic cell. A typical cell might consists of two pieces of metal, one zinc and the other copper. (Stephen K. Lower; March 8, 2005).

#### 1.2 Research Problem

Study of the effect of laser texturing on electrochemical cell electrode in the performance of electrochemical cells.

# 1.3 Objectives

The main goal of this research is to study the effect of laser texturing of electrode in electrochemical cell performance, laser processing for increasing the active surface area and study Interaction of laser with metals.

## 1.4 Literature Review

In 2016 Wilhelm Pfleging, Melanie Mangang, Yijing Zheng, and Peter Smyrek established different types of laser processing for increasing the active surface area 'laser-assisted self-organizing structuring' and 'direct structuring' of electrodes. The first of these processes can be applied to thin films and thick film electrodes that have small electrode footprint areas (coin cells). The second process is suitable for small and large electrode footprint areas (pouch cells). They used excimer laser ablation at a wavelength

of 248nm to produce self-organized surface structures on lithium cobalt oxide and lithium nickel manganese cobalt oxide (NMC) thick- and thin-film electrodes. They found that the active surface area could be increased by a factor of 10. They also used direct laser structuring—either with a 200ns fiber laser or an ultrafast fiber laser (380fs)—to form 3D micro structures Improved cycle lifetimes and increased capacity retention .

Alex .Neale, Yang Jin, Jinglei Ouyang, Stephen Hughes, In 2014 David Hesp, Vinod Dhanak, Geoff Dearden, Stuart Edwardson, Laurence. Hardwick, studies described the preparation and analysis of laser microstructured nickel metal electrodes for application as a cathode material in micro-batteries based on the nickel oxyhydroxide chemistry. Using ultra-short pulse length lasers (picoseconds to femtoseconds); surface micro-structures in the form of ripples were rapidly generated at the surface of nickel metal These cathodes. ripple micro-structures, with a periodic approximately equal to the wavelength of laser radiation used, are more commonly referred to as laser-induced periodic plasmonic structures (LIPPS). The electrochemical activity of the LIPPS nickel metal cathodes is investigated in aqueous KOH using cyclic voltammetry.

In 2007 Ulrich Muecke, Kojiro Nickel oxide x (NiO/CGO) films were deposited by spray pyrolysis and pulsed laser deposition on polished CGO electrolyte pellets. The thicknesses of the as-deposited films were 500–800 nm. The sprayed films showed a homogeneously distributed nano-grain sized microstructure after annealing in air whereas the PLD films exhibited a texture with elongated columnar grains oriented perpendicular to the substrate surface. The electrochemical performance of the Ni/CGO cermet thin film anodes was measured in a symmetrical anode/electrolyte/anode configuration in a single gas atmosphere setup by impedance spectroscopy. The polarization resistance of 60/40 vol.% Ni/CGO spray pyrolysed films

decreased with decreasing grain size and was 1.73 and  $0.34\Omega\cdot\text{cm}2$  for grain sizes of 53 and 16 nm, respectively, at 600 °C in 3% humidified 1:4H2:N2. The activation energy was 1.45 and 1.44 eV in the temperature range of 400–600 °C. The performance of the 49/51 vol.% Ni/CGO PLD cermet film was comparable to the spray pyrolysis films and was  $0.68\Omega\cdot\text{cm}2$  at 600 °C with an activation energy of 1.46 eV. The electrochemical performance was similar to state of- the-art thick film anodes and the Ni/CGO thin film cermets are promising candidates as electrodes in micro solid oxide fuel cells.

# 1.5 Thesis Lay Out

This is consists of four chapters, chapter one introduction and literature review and chapter two consist of basic concepts of laser and electrochemical cell and laser interaction with Metal, chapter three consist of experimental part(the materials and device and method), chapter four consists of result and discussion, conclusion and recommendations and finely the references.

# **CHAPTER TWO**

# **Basic Concepts**

#### 2.1 Laser:

Laser is an acronym for light amplification by stimulated emission of radiation. (A.Siegman, 1986).

The first laser was built in 1960. A laser differs from other sources of light in that it emits light coherently. Spatial coherence allows a laser to be focused to a tight spot. Spatial coherence also allows a laser beam to stay narrow over great distances .Lasers can also have high temporal coherence which allows them to emit light with a very narrow spectrum, i.e., they can emit a single color of light, the spatial and temporal coherence makes the difference between a laser and a light bulb .A lamp emits uncorrelated wave trains into all spatial directions. A laser generates coherent waves and the waves can have a high directionality. (The possibilities of generation of spatially and temporally coherent waves). A laser can generate a coherent continuous wave or a coherent pulse train. Extreme cases of generation of visible radiation are as follows:

- 1. The continuous wave laser (CW laser) emits a continuous electromagnetic wave. The field is spatially and temporally coherent.
- 2. The femtosecond laser emits an electromagnetic wave consisting of a pulse train. The duration of a single pulse of a train can be as short as 5 fs (1 fs = 1 femtosecond =  $10^{15}$  s). The field of a pulse train is spatially and temporally coherent too. Beside continuous wave lasers and femtosecond lasers, there are pulsed lasers. Producing laser pulses with durations in the

picosecond, nanosecond, microsecond, or millisecond ranges. (K.F. Renk, 2012). (Steen, W. M. 1998).

### 2.1.1 Laser Principle

Laser radiation is generated by stimulated transitions in an active medium (Figure 2.1). The active medium is a gain medium ,propagation of radiation in the active medium results in an increase of the energy density of the radiation. The active medium in a laser experiences feedback from radiation stored in a laser resonator. A portion of radiation coupled out from the resonator represents the useful radiation.

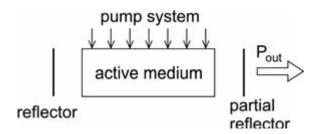


Figure (2.1) Components Of A Typical Laser

## a. The optical resonator:

The laser resonator has the task to store a coherent electromagnetic field and to enable the field to interact with the active medium. The active medium experiences feedback from the coherent field. We will describe resonators that consist of two mirrors one is a reflector of a reflectivity( $r_1$ ) and the other is a partial reflector serving as output coupler. The output coupling mirror has a reflectivity ( $r_2$ ) that also can have a value near 1 but that can be much smaller, semiconductor lasers can have reflectors with  $r_1 = r_2 \sim 0.3$ . Each type of laser requires its own resonator design. (K.F. Renk,2012).

#### b. Active medium ( a gain medium )system.

The gain medium is a material with that allows it to amplify light by way of stimulated emission. Light of a specific wavelength that passes through the gain medium is amplified (increases in power). For the gain medium to amplify light, it needs to be supplied with energy in a process called pumping.

#### c. Pumping System.

The energy is typically supplied as an electric current or as light at a different wavelength. Pump light may be provided by a flash lamp or by another laser.

(Gould, R. Gordon, 1959). (The Ann Arbor, 18 June 1959).

## 2.1.2 Laser Types

Lasers are characterized according to the physical state of the active material we call them solid-state, liquid, or gas lasers.

#### a. Solid Laser

Solid state lasers (except lasers). The active medium consists of ions in a dielectric solid; solid state lasers operated at room temperature, are available in the visible and the near infrared. Stimulated transitions between electronic states of ions give rise to generation of laser radiation.

#### b. Gas Laser

The active medium consists of atoms, ions, or molecules in gases. Gas lasers are available in the UV, visible, NIR FIR, and microwave ranges, (the excimer and the CO<sub>2</sub> laser, helium and helium-neon, He Ne, are the most common gas lasers).

#### **Carbon Dioxide Lasers**

Because of their ability to produce very high power with relative efficiency; carbon dioxide (CO<sub>2</sub>) lasers are used primarily for materialsprocessing applications. The standard output of these lasers is at 10.6 mm, and output power can range from less than 1w to more than 10 kw .Unlike atomic lasers CO2 lasers work with molecular transitions (vibrational and rotational states) which lie at low enough energy levels that they can be populated thermally and an increase in the gas temperature, caused by the discharge, will cause a decrease in the inversion level, reducing output power. To counter this effect high-power CO<sub>2</sub> lasers use flowing gas technology to remove hot gas from the discharge region and replace it with cooled (or cooler) gas. with pulsed CO<sub>2</sub> lasers that use transverse excitation, the problem is even more severe because, until the heated gas between the electrodes is cooled, a new discharge pulse cannot form properly. Avariety of types of CO<sub>2</sub> lasers are available. High-power pulsed and cw lasers typically use a transverse gas flow with fans which move the gas through a laminarflow discharge region into a cooling region, and back again .Low-power lasers most often use waveguide structures, coupled with radio-frequency excitation, to produce small, compact systems.

#### c. Semiconductor lasers

Semiconductor lasers (bipolar semiconductor lasers). Semiconductor lasers are solid state lasers that make use of conduction electrons in semiconductors. It are available in the visible, near UV and NIR spectral ranges and are being developed for the FIR. Stimulated transitions are either due to electronic transitions between the conduction band and the valence

band of a semiconductor in bipolar lasers or between sub bands of a conduction band in quantum cascade lasers. (Karl F, Basics of Laser Physics).

#### d. Liquid Laser

A liquid-crystal laser is a laser that uses a liquid crystal. The lasing medium is usually a dye doped into the liquid crystal. Liquid lasers are similar to the solid state lasers in that they consist of a host material (in this case a solvent such as alcohol) in which the laser (dye) molecules (such as rhodamines or coumarins) are dissolved at a concentration of one part in ten thousand. Dyes exhibit a very high degree of fluorescence, i.e., when the dye is exposed to ultraviolet light, it glows with characteristic color depending on the nature of the material. Different dyes have different emission spectra or colors. As a result, dye lasers cover a broad wavelength range from the ultraviolet at 320 nm to the infrared at about 1500 nm, a unique property of dye lasers is the broad emission spectrum (typically 30-60 nm) over which the gain occurs. when this broad gain spectrum is combined with a diffraction grating or a prism as the cavity mirrors, the dye laser output can be a very narrow frequency beam (10 GHz or smaller). Frequency tuning over even larger ranges is accomplished by inserting different dyes into the cavity. (Jacobs; Cerqua; Marshall; Schmid; Guardalben; Skerrett ,1988).

#### 2.1.3 Properties Of Laser Beams

Laser radiation is characterized by an extremely high degree of monochromaticity, coherence, directionality, and brightness. We can add a fifth property, which refers to the capability of producing very short light pulses, a less fundamental but nevertheless very important property. We now consider these properties in some detail.

## a. Monochromoticity

This property is due to the following two circumstances only an em wave of frequency since a two-mirror arrangement forms a resonant cavity oscillation can occur only at the resonance frequencies. The latter circumstance leads to an often much narrower laser line width (by as much as 10 orders of magnitude) than the usual line width of the transition as observed in spontaneous emission.

#### b. Directionality

Radiation comes out of the laser in a certain direction, and spreads at a defined divergence angle. This angular spreading of a laser beam is very small compared to other sources of electromagnetic radiation .The beam is almost parallel, and can be send over long distances.

#### c. Coherency

Laser radiation is composed of waves at the same wavelength, which start at the same time and keep their relative phase as they advance. So when two or more laser radiations can interfere each other ,so laser radiation has a coherency.

## e. Brightness

While summing up the discussion on monochromaticity (narrow line width) and directionality (low divergence) of laser, radiance of laser cannot be missed out. It is defined as the power emitted per unit surface area per unit solid angle. The units are watts per square meter per steradian. A steradian is the unit of solid angle, which is three-dimensional analogue of on ventional two-dimensional (planar) angle expressed in radians.(John Ambroseo, 2001).

## 2.1.4 Laser Applications

#### a. Industrial

Now include many new procedures, such as laser welding, drilling, cutting (e.g., glass decoration, trimming and milling) and other.

#### b. In medicine

Surgical treatment, vision treatment, dentistry, hair removal, skin treatment tattoo removal, etc.

#### c. In the military

Missile guidance, radar replacement, target guidance, etc.

#### d. In electronics

CDs, DVDs, laser printers, holograms, barcode scanners. (P.S. Zory, 1993).

#### 2.1.5 Laser Metal Interaction

Lasers have reached a high level of maturity and acceptance in industry. It is used for cutting, drilling, welding, forming, engraving, marking, hardening and various forms of surface treatment of metals in a broad spectrum of modern industries, including the automotive and aerospace industries, the shipbuilding industry, the microelectronics industry and the medical instrument industry to name a few. Laser metal processing is the Nd:YAG laser (the other one being the Co<sub>2</sub>), operating in the near infrared just outside the visible wavelength region. The YAG laser (or the similar in wavelength (color) Nd:YLF laser) is used routinely to cut and weld metals, metallic alloys and ceramics .The amount of transformed energy is determined by the light absorption mechanisms in the metal. Laser absorption in a metal depends on a number of different parameters, involving both the laser and the metal. The wavelength (or color) of the light, the angle with which the beam impinges on the metal surface and the polarization of the beam. The interaction of electromagnetic radiation with the free electrons in metals is so strong that the penetration depth of radiation is limited to a few wavelengths (referred to as skin depth). Typically, the absorption coefficient of metals from the near UV through visible (VIS) and near IR spectral range is between 105 and 107 cm a high absorption also implies ,a high reflectivity. Thus the reflectivity of metals over UV through the VIS spectral region ranges between 0.25 and 0.95. In the IR typical values are between 0.9 and 0.99. In contrast, reflectivity decreases considerably at wavelengths below 300 nm because the electrons cannot respond to the high frequency of the UV light. Certain metals such as gold and copper present, in addition, selective absorption (related to excitation of electrons in d-orbital) and, therefore, selective reflection (which is in fact responsible for the characteristic color of these metals). (Jenkins, F.A. and White, H.E., 1976).(Young, H.D, 1976).( Hecht, 1987).

# 2.1.6 Material Reflectivity

Material reflectivity by reducing the wavelength from 1064nm to 532nm, the reflectivity of copper and other conductive materials 1400-10<sup>6</sup> nm, the reflectance of metals keep in increasing until even more than 90%, for the most polished surfaces, then the utmost attention must be paid to this kind of materials when they are located near to laser equipments.

Table(2.1) Copper Reflectivity.

Material	1064nm	532nm
Copper	90%	45%

(Geoff shannon and paul severloh, January 2009).

# 2.2 Electrochemical Cell

An electrochemical cell is a device that converts electrical energy from chemical reactions or facilitating chemical reactions through the introduction of electrical energy. A battery consists of two or more cells connected in either parallel or series pattern. An electrochemical cell contains two strips made of different materials. The strips are called electrodes. The electrodes are suspended in a third material called the electrolyte, which interacts chemically with the electrodes to separate charges and produce a flow of electrons from the negative terminal to the positive terminal.

(Murray, J.B., Seyhan, A.A., Walter, N.G., Burke, J.M. and Scott, W.G, 1998)

#### 2.2.1 Batteries

Batteries are referred to as electrochemical due to the fact that they store electrical energy in the form of chemical energy. Batteries are galvanic cells or a group of galvanic cells connected in series. Where the total battery potential is equal to the sum of the potentials of the individual cells. There are three types of batteries - primary batteries, secondary batteries, and the fuel cell. Primary batteries are not re-chargeable, where as secondary batteries are rechargeable. Fuel cell will last as long as there is an ample supply of fuel to provide the energy. Batteries provided the main source of electricity before the development of electric generators and electrical grids around the end of the 19th century. Successive improvements in battery technology facilitated major electrical advances, from early scientific studies to the rise of telegraphs and telephones, eventually leading to portable computers, mobile phones, electric cars, and many other electrical devices. Scientists and engineers developed several commercially important types of battery. (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010).

# 2.2.2 Battery Development

#### a. Allesandro Volta 1782

His "Voltaic pile", a stack of zinc and silver disks separated by a wet cloth containing a salt or a weak acid solution, was the first battery known to Western civilization.

#### b. Humphry Davy 1813

Davy builds a 2000-plate battery that occupies 889 square feet in the basement of Britain's Royal Society. His earlier batteries provided power for the first public demonstration of electric lighting (carbon arc).

#### a. Michael Faraday, 1830's

Faraday discovered the fundamentals of galvanic cells and electrolysis that put electrochemistry on a firm scientific basis.

#### b. 1836 - Daniell cell

The Daniell cell is a type of electrochemical cell invented in 1836 by John Frederic Daniell, a British chemist and meteorologist, and consisted of a copper pot filled with a copper sulfate solution, in which was immersed an unglazed earthenware container filled with sulfuric acid and a zinc electrode. The Daniell cell was a great improvement over the existing technology used in the early days of battery development. A later variant of the Daniell cell called the gravity cell or crowfoot cell was invented in the 1860s by a frenchman named callaud and became a popular choice for electrical telegraphy .The Daniell cell is also the historical basis for the contemporary definition of the volt, which is the unit of electromotive force in the International system of units. Electromotive force of the Daniell cell would be about 1.0 volts. With contemporary definitions, the standard potential of the Daniell cell at 25 °C is actually 1.10 v. Figure 2.3 in the Daniell cell, copper and zinc electrodes are immersed in a solution of copper(II) sulfate and zinc sulfate respectively. At the anode, zinc is oxidized per the following half reaction:

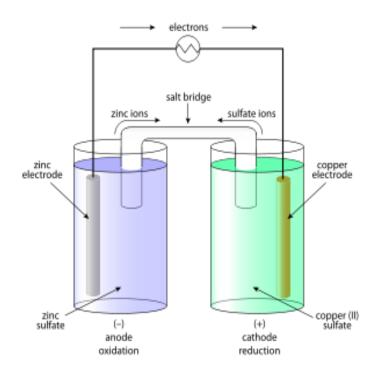


Figure (2.3) Daniell Cell

the two half-cell form of the Daniell cell

 $Zn(s) \rightarrow Zn2+(aq) + 2e-..$  (standard electrode potential -0.7618 V).

at the cathode, copper is reduced per the following reaction:

Cu2+(aq) + 2e-  $\rightarrow$  Cu(s) . . (standard electrode potential +0.340 V ).

the total reaction being:

$$Zn(s) + Cu2+(aq) \rightarrow Zn2+(aq) + Cu(s)$$
... (open-circuit voltage 1.1018 V).

the two half cells each support one half of the reaction s described above. wire and light bulb may connect the two electrodes. Electrons that are "pulled" from the zinc anode travel through the wire .The two half cells must be connected in a way that will allow ions to move freely between them. a porous barrier or ceramic disk may be used to separate the two solutions while allowing the flow of sulfate ions. When the half cells are placed in two entirely different and separate containers, a salt bridge is often used to

connect the two cells. The salt bridge typically contains a high concentration of potassium nitrate (a salt that will not interfere chemically with the reaction in either half-cell). In the above wet-cell during discharge, nitrate anions in the salt bridge move into the zinc half-cell in order to balance the increase in Zn2+ ions. At the same time, potassium ions from the salt bridge move into the copper half-cell in order to replace the Cu2+ ions being discharged.

(Borvon, Gérard ,September 10, 2012). (Hamer, Walter J,January 15, 1965). (Spencer, James N.; Bodner,George M.; Rickard, Lyman H. ,2010).

#### c. 1859 - Gaston Planté (French)

Invents the first lead-acid storage cell which consisted of two sheets of lead separated by a rubber sheet, rolled into a spiral and immersed in dilute sulfuric acid.

#### d. 1866 - Georges Leclanché (French)

By 1868 twenty thousand Leclanché cells were being used in telegraph systems. The original Leclanché cells were built in porous pots which were heavy and subject to breakage. Within twenty years other inventors had modified the design into what we now know as "dry cells" which became widely used in the first flashlights (1909) and in battery-powered radios of the 1920.

#### e. Thomas Edison

Development of the first practical lead-acid storage cell. The major improvement over Planté's design was the addition of a paste of PbSO4 to the positive plate. Edison, who was as much a chemist as an all-around inventor, thought that the lead in Planté-type cells made them too heavy, and that having acid in contact with any metal was an inherently bad idea. After much experimentation, he developed a successful alkaline battery. The

Edison cell uses an iron anode, nickel oxide cathode, and KOH electrolyte. This cell is extremely rugged and is still used in certain industrial applications, but it was never able to displace the lead-acid cell as Edison had hoped.

#### f. 1949 - Alkaline dry cell - Lew Urry (Eveready Battery Co.)

First commercial alkaline dry cell; These substitute KOH for the corrosive NH4Cl used in the older dry cells and last 5-8 times longer.

#### g. (Ruben and Mallory, 1950)

This was one of the first "button"-type cells which were widely used in cameras and hearing aids. The constancy of the 1.34 v output made them popular for use in sensitive instruments and cardiac pacemakers. The net cell reaction is

$$Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$$

most countries have outlawed sales of these cells in order to reduce mercury contamination of the environment.

#### h. NiCad

The NiCad cell quickly become one of the most popular rechargeable batteries for small consumer devices. They can deliver high current and undergo hundreds of charge–discharge cycles. Because cadmium is an environmental toxin, their use is being discouraged.

## i. 1959 - Fuel cell - Francis Bacon (UK)

The first practical fuel cell was developed by British engineer Francis Bacon (1904-1992). This hydrogen-oxygen cell used an alkaline electrolyte and inexpensive nickel electrodes.

#### j. Late Nicke I-metal hydride cells 1960

The hydride ion H– would be an ideal cathode material except for the fact that its oxidation product H2 is a gas. The discovery that certain compounds such as LiNi5 and ZrNi2 can act as "hydrogen sponges" made it practical to employ metal hydrides as a cathode material. One peculiarity of Ni-MH cells is that recharging them is an exothermic process, so that proper dissipation of heat must be allowed for. These batteries are widely used in cell phones, computers, and portable power tools. The electrode reactions take place in a concentrated KOH electrolyte:

Cathode (+): NiOOH + 
$$H_2O$$
 +  $e \rightarrow Ni(OH)_2 + OH$ 

Anode (-): 
$$(1/x) MH_x + OH \rightarrow (1/x) M + H_2O + e$$

#### 1990s - Lithium cells .

Lithium is an ideal anode material owing to its low density and high reduction potential, making Li-based cells the most compact ways of storing electrical energy. Lithium cells are used in wristwatches, cardiac pacemakers and digital cameras. Both primary (non-rechargeable) and rechargeable types have been available for some time. More recent applications are in portable power tools and perhaps most importantly, in electric-powered or hybrid automobiles.(advanced battery development)(2014).

Modern lithium cells operate by transporting Li+ ions between electrodes into which the ions can be inserted or intercalated. Cathodes are lithium transitionmetal oxides such as LiCoO3, while anodes are lithium-containing carbon, LiC6. (Nickel-Hydrogen, 2009-03-18. Retrieved 2012-08-29).

#### 2.2.3 Batteries uses

- a. electrical appliances such as cell phones (long-life alkaline batteries).
- b. digital cameras (lithium batteries).
- c. hearing aids (silver-oxide batteries).
- d. digital watches (mercury/silver-oxide batteries).
- e. military applications (thermal batteries).

# 2.2.4 Lithium batteries as incendiary devices

There have been numerous reports of fires and explosions associated with lithium batteries. In 2006, the dell corporation had to recall 4.1 million sony batteries that had been shipped with dell's laptop computers and were judged to be at risk owing to a manufacturing defect. This illustrates the difficulty of concentrating a large amount of chemical energy into a small package, which is of course the goal of all battery developers eager to meet commercial demands ranging from consumer personal electronics to electrically-powered cars. The fully-charged Li<sup>+</sup> deficient lithium cobalt oxide cathodes are inherently unstable, held in check only by a thin insulating membrane which, if accidentally breached, can lead to thermal runaway involving gaseous oxygen, carbon, organic solvents, and (in some cases) lithium chlorate all the components necessary for a fierce fire. Much research has gone into the development of fail-safe membranes. (Stephen Lower, 2005).

#### 2.2.5 Batteries Effect in the Environmental

Batteries are identified as a problem material in the waste stream. batteries are made from a variety of chemicals to power their reactions. some of these chemicals, such as nickel and cadmium, are extremely toxic

and can cause damage to humans and the environment. (Copyright Clean Up Australia, 2009).

# 2.2.6 Calculation the percentage surface area of Batteries(cell).

Percentage = (space after the increase - space before the increase) / (space before the increase)\*100%. (Bennett, Jeffrey; Briggs, William ,2005).

#### 2.2.7 Electrochemical cells consist of two electrodes

#### a. An anode

The anode is where the oxidation reaction takes place.

#### b. Cathode

The cathode is where the reduction reaction takes place.

Cu(s) + Zn<sup>+2</sup>
$$\leftrightarrow$$
Cu<sup>+2</sup>+ Zn(s)  
Cu(s)  $\leftrightarrow$ Cu<sup>+2</sup>+ 2e-(oxidation)  
Zn<sup>+2</sup>+ 2e- $\leftrightarrow$ Zn(s) (reduction)

# 2.2.8 Types of electrochemical cells

- **a.** Galvanic cell: electrochemical cell in which electricity is produced as a result of a spontaneous reaction (e.g., batteries, fuel cells).
- **b.** Electrolytic cell: electrochemical cell in which a non-spontaneous reaction is driven by an external source of current.

(Murray, Seyhan, Walter, Burke, And Scott, W.G,1998).

#### 2.2.9 Oxidation process

Oxidation is the loss of electrons or an increase in oxidation state by a molecule, atom, or ion.

# 2.2.10 Reduction process

Reduction is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.( Haustein, Catherine Hinga ,2014).

the figure(2.2) two half-cells are connected by a salt bridge, which prevents free mixing of both electrolyte solutions but permits the proper movement of ions to maintain electrical neutrality. The proper cell notation for the above cell Is Zn/ZnSO4 II CuSO4/Cu where / represents the boundary between the solution and the electrode and II represents the salt bridge separating the two compartments.

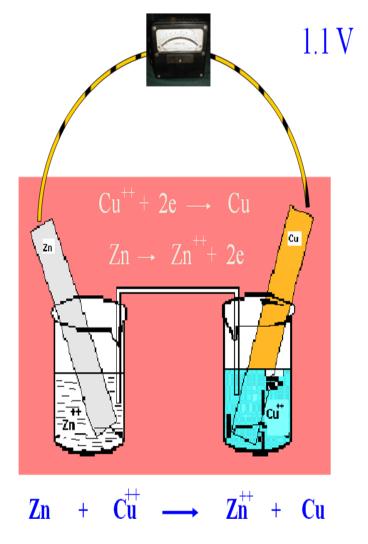


Figure (2.2) Half-Cells

# **2.2.11 Voltage**

The theoretical standard cell voltage,  $E_0$  (cell) can be determined using the electrochemical series and is given by the difference between the

standard electrode potential at the cathode,  $E_0$ (cathode), and the standard electrode potential at the anode,  $E_0$ (anode) as  $E_0$ cathode -  $E_0$ anode =  $E_0$ cell . The standard electrode potential,  $E_0$  for an electrode reaction, written (by convention) as a reduction reaction (i.e., involving consumption of electrons) is the potential generated by that reaction under the condition that the reactants and the products are in their standard state in relation to a reference electrode, (a reactant or product is defined to be in its standard state when the component in a condensed phase is at unit activity and any component in the gas phase is at a partial pressure of 1 atmosphere). University of Cambridge (2005).

# **CHAPTER THREE**

# **Experimental Part**

#### 3.1 Introduction

This chapter includes the materials used in this work and the following methods (sample preparation and setup) and the procedure.

#### 3.2 Materials

#### a. Zinc Electrode:

High-purity zinc (99%) foils with a thickness of 500 µm were used in the preparation of the zinc electrodes, with area of 12.25 cm². The laser spot was scanned across the planar zinc surface in two parallel lines in1mm. The ability of a zinc-based energy storage device to store and deliver power relies on the amount of the electrochemically active material that can accumulate at the electrode/electrolyte interface.

It represents the cathode in the electrochemical cell figure (3.1).



а



b

Figure(3.1) Zinc Electrode (a) Unirradiated (b) Irradiated

# b. Copper Electrode:

High-purity Copper (99.5%) foils with a thickness of 200µm were used in the preparation of the Copper electrodes .With area of 12.25 cm<sup>2</sup>. It represents a positive electrode in an electrochemical cell figure (3.2).



Figure (3.2) Copper Electrode

#### c. Zinc Sulfate

Zinc sulfate is the inorganic compound with the formula ZnSO<sub>4</sub> with molaraty of 1M and wight 50g .

# d. Copper (II) Sulfate

Copper (II) sulfate, also known as cupric sulfate, or copper sulphate, is the inorganic compound with the chemical formula CuSO<sub>4</sub> concentration= 1M.

#### 3.3 Devices

#### a. CO<sub>2</sub> laser

Carbon dioxide lasers are the highest-power continuous wave . D1310 CO<sub>2</sub> laser cutting machine was used here. The CO<sub>2</sub> laser produces a beam of infrared light with the principal wavelength bands centering on 9.4 and 10.6 micrometers (10600nm). These are one of the most common types of laser, are used for many different applications, and maximum output power 90watt figure(3.3). The laser spot was scanned across the planar zinc surface in parallel lines at a predefined scan rate (10mm<sup>-1</sup>)



Figure(3.3)CO<sub>2</sub> Laser Device

## b. A salt bridge

A salt bridge figure (3.4), in electrochemistry, is a laboratory device used to connect the oxidation and reduction half-cells of the galvanic cell (voltaic cell). It maintains electrical neutrality within the internal circuit, preventing the cell from rapidly running its reaction to equilibrium. If no salt bridge were

present, the solution in one half cell would accumulate negative charge and the solution in the other half cell would accumulate positive charge as the reaction proceeded, quickly preventing further reaction, and hence production of electricity and the type of the salt inside the bridge K<sub>2</sub>SO<sub>4</sub>.



Figure (3.4) A Salt Bridge Device

#### 3.4 Method

Electrochemical measurements were obtained using two-electrode cell equipped with the zinc working electrode, a copper electrode, K<sub>2</sub>SO<sub>4</sub> was use as the electrolyte in a salt bridge. The voltage of the Electrochemical Cells was measured every one minute using planar zinc electrode ,and then using Textured zinc electrode with different electrolyte figure (3.5).

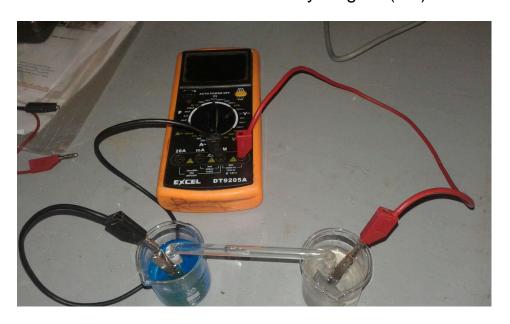


Figure (3.5) Electrochemical Cells

## CHAPTER FOUR

# **Results and Discussion**

#### 4.1 Introduction

This chapter summarizes results obtained during the work. Results include photographs, Figures and tables as shown below. Data fitting of experimental results was also shown, in addition discussion and conclusion.

#### 4.2 Results

The laser-processed area of the zinc strip was observed to reflect infrared light differently compared to the planar unprocessed area, making it apparent which section of the metal had been laser treated .The results in table (4.1) showed the voltage and time of electrochemical cell consisting of Zn/ZnSO4 II CuSO4/Cu for the planer zinc cathode .

The results in table (4.2) showed the voltage and time of electrochemical cell consisting of Zn/ZnSO4 II CuSO4/Cu. After texturing cathode (Zn) with a wavelength10600 nm from IR rang and energy 90watt and speed 10mm/s.

Table(4.1) Results of the voltage of the Electrochemical Cell Before Texturing Cathode (Zn)( With Planar Cathode).

Voltage (mv)	Time(Minutes)
0.955	0
0.908	1
0.873	2
0.872	3
0.870	4
0.869	5
0.866	6
0.863	7
0.860	8
0.857	9

Table(4.2) The Results of the Voltage of The Electrochemical Cell After Texturing Cathode (Zn).

Voltage(mv)	Time(Minutes)
1.085	0
1.074	1
1.068	2
1.063	3
1.050	4
1.042	5
1.031	6
1.019	7
1.011	8

1.007	9

The results show considerable increase in voltage of electrochemical cell (more surface area) after texturing cathode (Zn) by CO<sub>2</sub> laser beam. The results of the electrochemical cell obtained in the time (in minute 0) using texturing cathode (Zn) showed high value of voltage but using planer cathode (Zn) showed ordinary values of voltage ,also in last time (in minute 9) using texturing cathode (Zn) the voltage highest than the first result before texturing. It would be expected that maximizing the accessible surface area of zinc cathode would create a larger area for active material accumulation, leading to improved energy storage performance. The produce thickening of the ZnOx over layer on zinc (Alex R, etal, 2014).

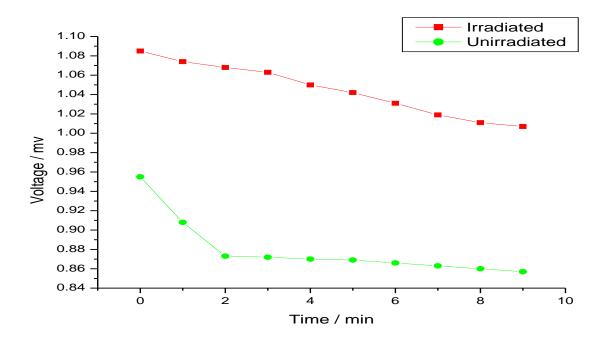


Figure (4.1) voltage- time curve of the electro chemical cell (red with Textured cathode-green with planar cathode)

Figure (4.1) shows variation in voltage with increase of time, the area under the curved for irradiated cathode(red curve) is 0.99101 and the area under the curved for unirradiated (green curve) is 0.97052. The area under the voltage curves indicating the total voltage of the two cells, the area of the total quantum yield before and after texturing increase by a factor 2.1% over the whole time operation. From this figure it can be seen that in the case of the electrochemical cell with irradiated cathode the slope is equal to 0.0087 which is mean that the performance is relatively stable from the begin time to the end. The case of the non-irradiated cell the curve is divided into two slopes from the first time to the third the slope is 0.041 and from the fourth time to the end the curve slope is equal 0.00178, it is observe that the second region is more stable than the first region or Irradiated cell.

## 4.3 Conclusions

In Conclusion the effect of the laser on improving the electrochemical cell performance was obtained ,it was found that irradiation of the cathode of the cell by carbon dioxide laser beam increase the cell surface area and leads to increased voltage. It has been reached to increase the cell performance by factor about 2.1%. It was observe that laser carbon dioxide does not effect the positive electrode of the cell (Cu) because of reflectivity of copper is 90% in IR.

#### 4.5 Recommendations

In the future works one can study the effect of laser in anode.

Study the relation of current and time.

Study determine the efficiency of Irradiated cell.

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