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Preparation and evaluation of the efficiency of nano composite thin film for the production of hydrogen gas

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Abstract

In this research had been studied the preparation and the study of the efficiency of Composites nano thin film for the production of electrodes used in the production of hydrogen gas through the Electrolysis cell consists of these Anode nano (Co: Mn, Wo3) either electrode cathode nano (NI. Cr .MO) In the water electrolysis process the hydrogen is produced by electrochemical splitting water molecules (H2O) into their constituent hydrogen (H2) and oxygen (O2). this thin films was prepared on glass substrates, also Aluminum oxide by using deposition . ..structured characteristics was studied through the analysis of X-ray diffraction (XRD) of the prepared film for determining the yielding phase which are to set the with standard tables . Also, the sample was tested atomic force microscope to identify the roughness of prepared films surface and the study of the efficiency of this cell to the electrode material, the distance between the electrodes, And has been the study of the volume of gas output ,voltages with change time and current.

Keywords: nano composite thin film, nano (Co: Mn, Wo3) , nano (NI. Cr .MO) , X-ray diffraction (XRD), production of hydrogen gas, atomic force microscope.

الخلاصة:

يركز هذا البحث على تحضر ودراسة كفاءة أغشية متراكبة نانومترية لإنتاج أقطاب كهربائية تستخدم في إنتاج غاز الهيدروجين وذلك من خلال استخدامها في خلية تحليل كهربائية النانويه حيث يصنع القطب الموجب من مادة الكوبالت ،المنغنيز وثلاثي التنكستن ، حيث هذه المواد لها سرعة تفاعل عالية عند القطب الموجب. ويحضر القطب السالب من النيكل ،الكروم والموليبدينيوم حيث يتم انتاج الهيدروجين بعملية الكهروكيميائية لتقسيم الماء الى هيدروجين وأوكسجين ، تم إعداد هذه الأقطاب على ركائز من الزجاج والنوع الاخر من اوكسيد الالمينيوم باستخدام عملية الترسيب ، وجرى دراسة الخصائص التركيبية ، من خلال تحليل حيود الأشعة السينية (XRD) للغشاء المحضر لتعيين الأطوار الظاهرة ومقارنتها مع الجداول القياسية لها. كذلك تم فحص الضوئي بمجهر القوى الذرية للتعرف على خشونة سطح الأغشية المحضرة ،تم دراسة كفاءة هذه الخلية للعوامل التالية مادة القطب، المسافة بين الأقطاب، وكذلك دراسة حجم الغاز مع تغير الفولتية ،التيار والزمن .

Introduction:

Hydrogen as a secondary energy carrier can play an important role in our future energy economy. Hydrogen can be stored, transported in tanks or pipe lines, is clean burning, and can be directly and efficiently converted into electricity using fuel cells. However, the major barrier is how to generate and supply pure hydrogen directly. One of the most efficient and simple ways to obtain hydrogen with high purity is the water electrolysis.[1] Hydrogen production techniques can be divided into four

categories: biological, chemical, electrochemical such as water electrolysis, halide electrolysis, and H2S electrolysis, and thermal technologies. [2,3] Water electrolysis history started with observations of Nicholson and Carlisle in 1800 [4]. There were around 400 industrial water electrolysis units on 1902 and first large water electrolysis plant with production capacity 10000 Nm^3/h was opened on 1939 [5]. High pressure electrolysers appeared some years later, but first industrial solid polymer electrolysis system was made by General Electric on 1966. High temperature solid oxide electrolysers were introduced in 1972, but first large alkaline electrolysis unit was built on 1978 [5]. Although the development of different water electrolysis systems are evident by walking through the time, their energy efficiency is still under 60% in operational mode, calculating on lower hydrogen combustion heat [6,7]. Today, nano structure semiconductor footnotes have attracted a significant attention due to their high electro-active surface, desire light harvesting property and ease of synthesis using low cost chemical Routes [8]. Recently, nano structured transition metal oxides have attracted a lot of attention due to their technological application sand outstanding properties. The properties (such asmagnetic, optic, catalytic, and electronic) of nano materials depend strongly on their size, structure, and shape. Co3O4nano particles exhibit weak ferromagnetic behavior. CoO nano crystals display super paramagnetism or weak ferromagnetism, where a sbulk CoO is antiferro magnetic[9, 10], WO3 films can be integrated as promising top layers inefficient multi junction hybrid photo electrode systems, providing an oxide/electrolyte interface where oxygen-evolution reactions take place. In these multi junction hybrid photo electrodes, the oxygen-evolving reaction takes place at the illuminated WO3/electrolyte interface, whereas hydrogen evolution occurs at the back surface "promoted by a suitable catalyst layer". However, the photo electrochemical response of WO3 has been scarcely reported when compared to investigations of TiO2. Therefore, studies directed toward optimization of the photo electrochemical response of the WO ground for technical exploration [11]. Synthesis and characterization of nano crystalline materials have recently gained much attention due to their unique properties. Nickel oxide (NiO) is a metal oxide semiconductor that has a wide range of technological applications [12]. Transition metal oxides like nickel oxides have found wide application such as: transparent electrode, efficient control of energy inflow-outflow of buildings or automobiles and aerospace, smart window, solar thermal absorber, electrodes for batteries, large scale optical switching glazing chemical sensors, electrochromic device [13].

Experimental detail:

Create rules were the rules used by quartz glass and Aluminum oxide by using deposition and has been cleaned to get rid of impurities or suspended matter, because the presence of these impurities affect the properties of the thin film of the record. Wash the glass substance with dilute hydrochloric acid and then leave it in ethanol for 10 minutes, then wash thoroughly with distilled water and then dried. the Aluminum substrate heat treatment (T = 400 ºC) for four hours, and to get rid of the

stresses in the plate during manufacturing operations For coarse grains For Terms of homogeneity for the growth of pores on large areas. Must clean aluminum substrate in the audio vibration device , A mixture of distilled water and acetone, acetic acid water. And dipping the aluminum substrate in a combination of chrome acid and phosphorus for 15 seconds , so as to obtain the nano-holes in the aluminum substrate.

1- Prepare the anode electrode:

Tin oxide has been resolved bilaterally with nano (Co: Mn, Wo3) and stirring for two hours ,The dissolution of the reactants complete dissolution, then deposition gelatin waving solution on glass substrates and substrates of oxide Porous aluminum. Were placed in the oven at class (80ºC) and then the samples taken out of the oven and left for 15min to cool ,The nano (Co: Mn, Wo3) powder was doped with (1wt%) Sn (99.99% purity) to powder . The thickness of films was 90 nm. is shown in Fig. (1a,1b,1c,1d,1e).

2- **Prepare the cathode electrode**:

Tin oxide has been resolved bilaterally with nano ((NI. Cr .MO) and stirring for two hours ,The dissolution of the reactants complete dissolution, then deposition gelatin waving solution on glass substrates and substrates of oxide Porous aluminum. Were placed in the oven at class (80ºC) and then the samples taken out of the oven and left for 15min to cool ,The nano ((NI. Cr .MO) powder was doped with (1wt%) Sn (99.99% purity) to powder . The thickness of films was 90 nm. is shown in Fig. (2a,2b,2c,2d,2e).

Characterization:

The surface morphology and grain size was carried out by using Atomic force microscopy AFM**,** XRD device , (XRD-6000 Shimadzu Japan) was used for the purpose of measuring this of crystalline structures formed in the samples. Where the target was CuKα radiation (λ=1.54oA) in the range of 2θ=10-60^{o}, We used the Barak law to calculate the distance (d) between the atomic levels.

$n\lambda=2d\sin\Theta$ (1)

Where: - n diffraction rank equal to (1).

Θ angle of diffraction.

λ : wavelength of X-rays. [14].

Stages were identified by comparing the values of the spaces formed between the levels after X-ray diffraction using standard tables (ASTM)..

Result and Discussion:

1- Results of an atomic force microscope

Atomic Force Microscopy (AFM) is capable of measuring surface structures with sub-angstrom resolution, making it an excellent method to precisely determine film thicknesses. An AFM uses a pointed probe at the end of a long arm or cantilever, similar to that of a record player, which can be used to "scan" a surface. In tapping mode, the probe is driven to oscillate in a plane normal to the sample surface. Pizza drivers are used to raster the oscillating probe across the surface, while the probe taps the surface. Signals from the detector are used to construct an image showing the

topography of the sample. The rapid annealing has a positive clear effect on prepared thin film oxide, as shown. In Fig. (3a,b) It was found that the root mean square (rms) of the surface roughness of the nano (Co: Mn, Wo3:Sn) anode electrode , nano (Ni. Cr .MO: Sn) cathode electrode And will be less volume of small blocks of atoms volatile matter precipitation electrode will be more increased annealing temperature.

2- X-Ray diffraction Results

An X-rays spectrum of deposit electrodes after the treatment is shown in figure (4a,b). It is found that the prepared films are polycrystalline structure with (110), (111), (001),(101)(110) and(001), (110), (101),(111)(110) ,plan refraction and this is consistent with research published previously, after comparing the with standard tables (ASTM). X-ray diffraction methods provide information on the crystalline states, chemical composition, crystallographic orientations and lattice parameters of the materials. Qualitative and quantitative evaluation of solid solutions, crystal size and preferred orientation of the films are also information which can be provided by x-ray diffraction.

3-After the preparation and study of nano electrodes characteristics were electrolytic cell design. As shown in Fig. (5a,5b). Electrolysis cell consists of these Anode nano (Co, Mn, Wo3) either electrode cathode nano(Ni. Cr .MO) In the water electrolysis process the hydrogen is produced by electrochemical splitting water molecules (H2O) into their constituent hydrogen (H2) and oxygen (O2). The decomposition of water takes place in a so called electrolysis cell and consists of two partial reactions that take place at two electrodes. The electrodes are placed in an ion-conducting electrolyte (usually an aqueous alkaline solution with 29 % potassium hydroxide KOH). Gaseous hydrogen is produced at the negative electrode (cathode) and oxygen at the positive electrode (anode)

Oxidation Describes the electrons (e^-) loss (or the protons gain) by a molecule, atom or ion. In water electrolysis, at the anode electrode (+) (oxygen production), the oxidation equation is:

$$2H_2O \rightarrow O_2 + 4H^+ + 4\,e^- \quad (2)$$

Reduction Describes the electrons (e^-) gain (or the protons loss) by a molecule, atom or ion. In water electrolysis, at the cathode electrode (-) (hydrogen production), the reduction equation is:

$$4\,H^+ + 4\,e^- \rightarrow 2\,H_2$$

For splitting the water molecule, the electric energy is consumed by the Redox chemical reaction. As consequent, the change in enthalpy ΔH, entropy ΔS (heat exchange=irreversible energy), and Gibbs energy (reversible energy) ΔG are closely related to the electric and the thermal energy generated by cell [15]. Assuming that the PEM electrolyser cell temperature T [K] is given in Kelvin, for the water splitting, the change in enthalpy can be given according to the following equation:

$$\Delta H = \Delta G + T\,\Delta S \quad (4)$$

According to this equation, the electrical and thermal behaviours are combined. From the view of point of the electrolyser destruction, the current and the temperature are very significant. In one hand, high current could cause: electrode destruction, membrane melting, membrane drying or electrode pressure augmentation [16]. In other hand, a high temperature could induce: membrane hot point and membrane tear. In addition, these faults could cause a H_2 (respectively O_2) migration to O_2 (respectively H_2) side. the amount of hydrogen produced is steadier in a specific period of time. At a voltage of 12 V both measurements taken are about the same with very slight differences . shows Table (1).

is obvious that as much as the voltage increases, the amount of hydrogen produced is steadier in a specific period of time, the measurements of the volume of hydrogen where taken having a constant voltage for one minute shows table (2) .

different amount of currents were applied and then the volume of hydrogen produced in each current was measured .The results from this experiment will show if the electrolyses produces the same amount of hydrogen when the same values of current are used shows table (3).

When studying the distance between the electrodes was found that the larger the distance between the large electrodes least hydrogen production, as well as the quality of the polarity affect the production of hydrogen found that the aluminum electrodes is more efficient than Glass electrode.

$$\text{Efficiency} = \frac{V_{Real}}{V_{ideal}} \times 100\% \qquad (2)$$

Equation 2 is the comparison of the actual hydrogen gas produced against the ideal value. Videal (cm3) is the hydrogen gas produced per unit of time read by the flowmeter and Videal (cm3) is the ideal volume of hydrogen gas generated, which can be calculated using the ideal gas law equation at the given conditions. The ideal volume.

Conclusion :

1- Through this study found that the aluminum electrode are more efficient than glass electrode
2- Notes the increase in the volume of gas to increase the voltage of the prepared samples, the largest of the films prepared on substrates of aluminum oxide films prepared him for the glass substrates.
3- Notes the increase in the volume of gas to increase the current of the prepared samples, the largest of the films prepared on substrates of aluminum oxide films prepared him for the glass substrates.

Note: The preparation of nanomaterials mentioned her search of the primary materials and optical properties study was published in the International Journal(IEEE explore / Page(s)26 - 30 Print ISBN: 978-1-4799-0713-7) as well as in the Conference University of technology, and University of Basra So I did not mention how to prepare these materials in this research.

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Fig.(1a): Nano WO3 substance Preparation

Fig.(1b): Nano co substance Preparation

Fig.(1c): Nano Mn substance Preparation

Fig.(1d) aluminum substrate

Fig.(1e) glass substrate

Fig.(2a): Nano Mo substance Preparation

Fig.(2b): NanoNi substance Preparation

Fig.(2c): Nano Cr substance Preparation

Fig.(2d) aluminum substrate

Fig.(2e) glass substrate

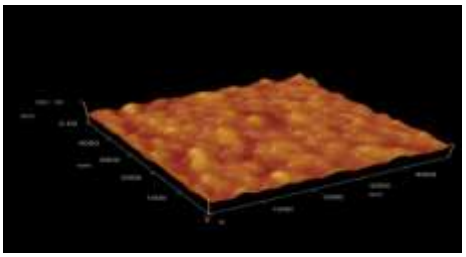


Fig. (3b) Atomic force microscope examination (cathode)

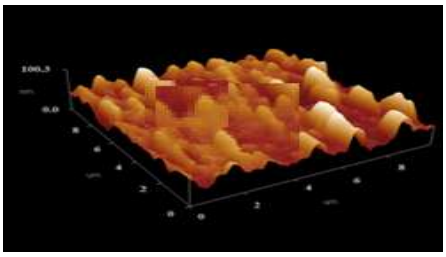


Fig. (3a) Atomic force microscope examination (anode)

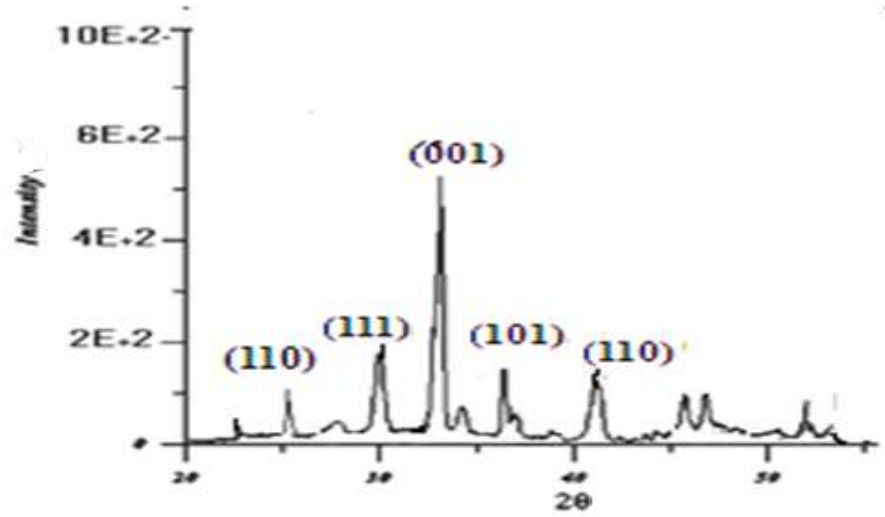


Fig. (4a): X-ray diffraction analysis nano(.Co, Mn, Wo3)

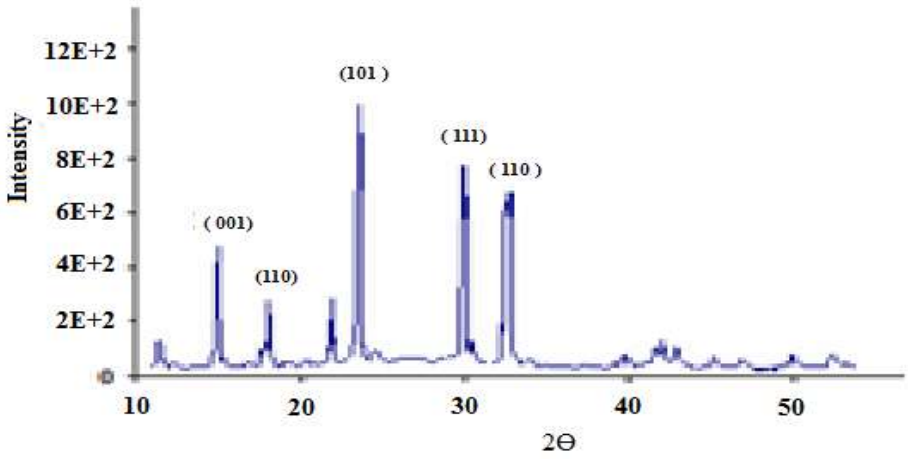


Fig. (4b): X-ray diffraction analysis nano(Ni. Cr .MO)

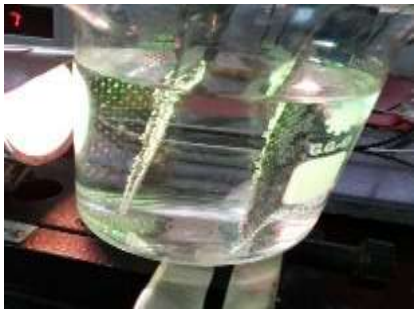


Fig. (5a) laboratory work shows hydrogen Production on nano electrode (glass)

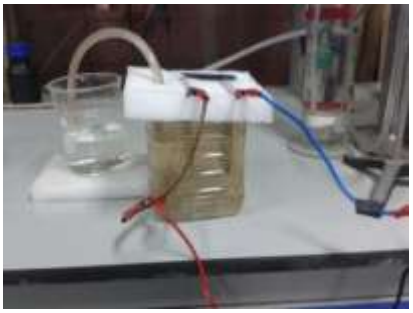
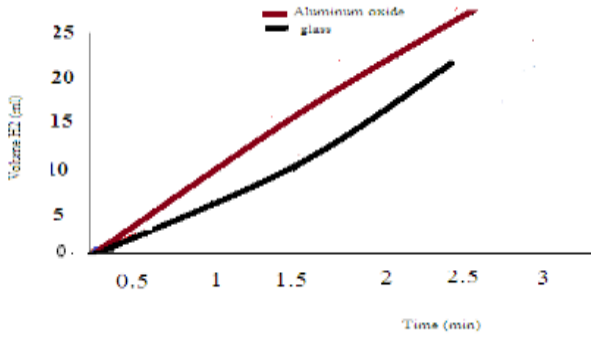


Fig. (5b) laboratory work shows hydrogen Production on nano electrode (Aluminum oxide)

table(1) shows the relationship between the volume of gas with time

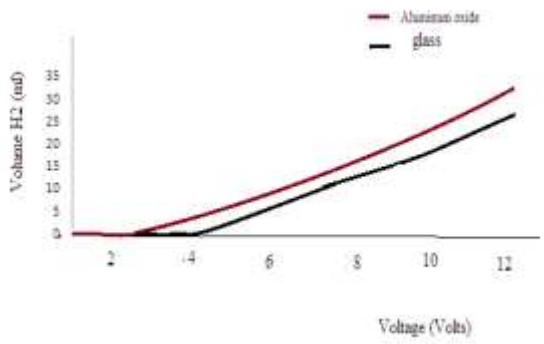
Volume H2 (ml)		Time (min)	Voltage (Volts))
Aluminum oxide	glass		
0	0	0	12
4.8	2	0.5	12
10.2	5	1	12
17	9.8	1.5	12
20.2	15.2	2	12
25.6	20.8	2.5	12



Fig(6) : Graph shows the relationship between Volume – time

table(2) shows the relationship between the volume of gas with voltages

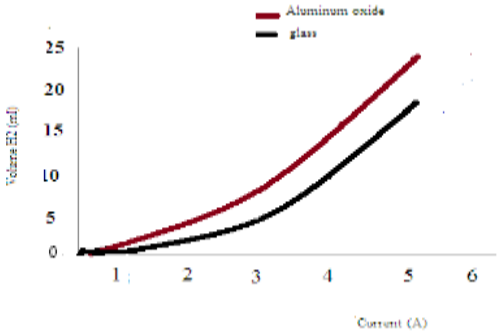
Volume H2 (ml)		Time (min)	Voltage (Volts)
Aluminum oxide	glass		
0	0	1	2
6	0	1	4
10.3	5.4	1	6
16.8	10.2	1	8
21	19	1	10
32	26	1	12



Fig(7) : Graph shows the relationship between Volume – Voltage

table(3) shows the relationship between the volume of gas with current

Volume H2 (ml)		Time (min)	Current (A)
Aluminum oxide	glass		
0	**0**	**1**	**0**
1.4	**0**	**1**	**1**
4.6	**2**	**1**	**2.4**
8	**4.7**	**1**	**3**
15.7	**9.9**	**1**	**4**
23.4	**18.8**	**1**	**5.1**



Fig(8) : Graph shows the relationship between Volume – current