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Production of High Purity Hydrogen from Magnesium Metal Reaction with Citric Acid in Seawater

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ABSTRACT

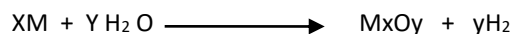
Citric acid with different concentrations ratios was studied to enhance hydrogen generation from magnesium metal powder- water reaction in both tap water and seawater. The amount of hydrogen generated was measured. Seawater was more efficiently in generating hydrogen gas without heating or adding any catalyst. By filling the gas- reactor with seawater and citric acid, the hydrogen produced from 30 – 90 minutes was rapid and/or regularly. The magnesium metal was recovered as pharmaceutical or as magnesium oxide crystals. The Prepared graphene oxide modified with increase in surface area by terminal oxygenated groups such as hydroxyl, epoxy and carbonyl successfully can be used as hydrogen storage material. These surface functional groups makes graphene oxide an excellent applicant for hydrogen storage. The HR - TEM analyses revealed hexagonal platelet aggregates and few curved tube-like graphene sheets. The SEM and EDX showed the surface morphology of magnesium citrate and magnesium oxide respectively. A comparison of DSC/TGA analyses of graphite, exfoliated graphene and graphene oxide shows more stability for graphene oxide. A Hydrogen volume generation correction is studied too.

Keywords: Hydrogen, magnesium, energy, seawater, characterization

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INTRODUCTION

Production of high purity hydrogen by irreversible reaction of magnesium with proton – containing compounds is considered simplest and accessible method to produce hydrogen as a fuel for portable source of electrical energy. Magnesium powder as a light metal exhibit high reaction rates as fuels are safe to store and transport and exhibit long shelf life [1]. Metal powder fuels do not have the storage and safety problems endemic to hydrogen, and represent an energy commodity which can be stored and traded, in a similar manner to solid, liquid and gaseous hydrocarbons.



Citric acid is a tribasic acid ensures complete and regular hydrogen generation in the reaction with magnesium powder but with high ratio HA\ mg(20% - 50%). Fortunately citric acid is a manufactured product. Using H₃PO₄, which reacts as semi basic acid, with Mg metal in 3:2 Mg/ HA ensures the complete hydrogen evolution [2]. Sulfuric acid reacts with magnesium as (dibasic), in this case the complete interaction depends on the concentration of sulfuric acid i.e. 98 g of H₂SO₄ (1 mol) produces 120 g of MgSO₄ (1 mol) dissolving in 12 : 355 = 0.338 liter of water. This means that the concentration must be < 22.5 wt % or the H₂ evolution ceases after interaction of last portion. Thus, hydrogen production during interaction of magnesium metal with organic acid like citric acid is economically compared to magnesium hydride by at least (4-5 times).

The maximum theoretical hydrogen yield that can be produced from each metal powder such as (B, Mg, Al, Si, Cr, Mn, Fe,Ni, Cu, Zn, Se, Zr, Mo, Sn, W) is present in [3] showing metals with lower potential produces larger amounts of hydrogen. The energy released from the metal-water cycle, composed of both the metal-water reaction heat and that released from combustion of the hydrogen production.

Hydrogen storage is one of the important issues that must be solved for a success full market. As high pressure and liquid storage of hydrogen is not a simple technology, so further opportunity for increasing hydrogen density at low pressure is solid state hydrogen storage [4]. Graphene has high surface area to weight ratio, it is strong, cheap, chemically inert, and environmentally benign. It is an ideal substrate for hydrogen storage. Graphene oxide (GO) has been used as an energy storage material such as, hydrogen-storage components [5]. More recently, exfoliated graphene and graphene oxide (GO) which consists of multiple surface functional groups such as (-RooH – RooH) and hydroxyls (-OH) as well carbonyls (-C=O) and carboxyl(-COOH) at the edges, shows an enhancement for adsorbate – adsorbent interaction leading to increase hydrogen storage capacity [6]. Graphene with oxygen – containing chemical groups has superior properties such as large surface area, mechanical stability, and tunable electrical and optical properties. More over the surface functional groups makes (GO) an excellent candidate in coordinating with other materials or molecules. (GO) has applications of energy storage / conversion and environmental protection, including hydrogen storage materials [7]. Graphene with high pore structures are functionalized for gas (H₂, CH₂, CO₂, N₂, NH₃, NO₂, H₂S, SO₂.....etc.) Sorption, storage, and separation [8]. Adsorption –desorption of hydrogen from metals can be performed first by reactive mechanical milling combined with hydrogen. To reduce particle agglomeration and overcome problem of oxidation associated with reactive mechanical milling, pulverization can be used. Hydrogen absorption measurements can be carried out by pressure – composition – temperature and thermogravimetric analysis. The SEM, TEM, X-rays can be effective for microstructure characterization. The FTIR and gravimetric analysis is true for desorption measurements [9-10].

This study aims to generate hydrogen [11] as renewable energy by reaction of magnesium with water and attempt to store hydrogen in different laboratory prepared nano materials. Both thermal and hydrogen energy would lead to economic benefit through job, wealth. A study for Magnesium recovery is shown too.

MATERIALS AND METHODS

Materials

Seawater composition: the main oxides present in seawater is shown in Table (1).

Magnesium metal powder analytical grade was used with organic acid as proton donor for hydrogen evolution during water reaction from 30 – 100 minutes.

Nano- graphene prepared in lab. by modified Hummers method, was treated with ozone and UV- light to increase the oxygenated groups for more hydrogen trapping through storage in solid materials.

Recovery of magnesium as pharmaceuticals or as magnesium oxide after hydrogen evolution and reaction completion.

Methods

Evolution of pure Hydrogen:

Magnesium metal powder (0.05 g, 0.1g and 0.5g) reacts with water and citric acid added in different ratios % (20%, and 50%) to water. Weights were loaded into the gas reactor and allowed to react for completion during 30-100 minutes. Generated hydrogen is about 99% purity without emissions of pollutants. The total volume of generated hydrogen was calculated by integrating the experimentally measured hydrogen generated rate over time (volumetric data) Fig (1). All experiments performed without stirring. A correction factor for hydrogen volume was studied as follows:

H₂ Volume Corrections

Volume of H₂ collected over water is measured on the container scale. However, the measured volume is affected by the water head difference causing a difference of pressure at which H₂ is collected. Accordingly, measured H₂ volume is different from its volume at atmospheric pressure. To correct this difference, the relation between H₂ volume and pressure was considered. With reasonable tolerance H₂ could be treated as an ideal gas with volume and pressure given as follows: -

$$PV = nRt \tag{1}$$

Where: -

- P Pressure (Pascal)
- V Volume (m³)
- n Number of moles
- R Universal gas constant = 8.3145 (J/mol K)
- t Temperature (K)

For the same no. of gas moles collected at the same temperature (t), result of volume (V) multiplied by pressure (P) is equal at different states, hence: -

$$P_{state1} V_{state1} = P_{state2} V_{state2} \tag{2}$$

For the current experiment: -

$$P_{atmospheric} V_{atmospheric} = P_{experiment} V_{measured} \tag{3}$$

Where :-

- P_{atmospheric} Atmospheric pressure = 1 Bar = 10.1972 m H₂O = 100000 Pascal
- V_{atmospheric} Volume at atmospheric pressure (m³)
- V_{measured} Measured gas volume (m³)
- P_{experiment} Experiment pressure that could be calculated as: -

$$P_{experiment} = P_{atmospheric} - \Delta P \tag{4}$$

Where: -

ΔP Pressure corresponding to liquid head difference, as shown in Figure 1

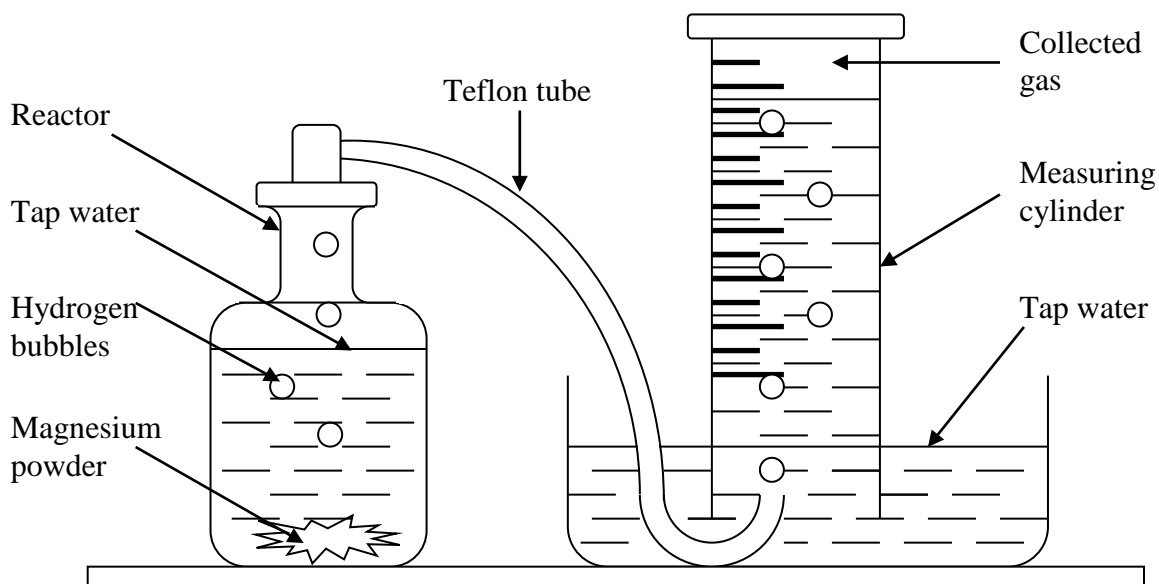
Accordingly, actual volume of H_2 at atmospheric pressure could be calculated as: -

$$V_{\text{atmospheric}} = V_{\text{measured}} \left[\frac{P_{\text{atmospheric}} - \Delta P}{P_{\text{atmospheric}}} \right] \quad (5)$$

Percentage of gas volume measurement error could be calculated as: -

$$V_{\text{error}} \% = \left[\frac{V_{\text{measured}} - V_{\text{actual}}}{V_{\text{actual}}} \right] * 100 \quad (6)$$

For the current setup the liquid head difference was 10 cm (water). Volume error percentage was evaluated for the current setup and was found to be less than 1%. Accordingly, it was decided to ignore the error. It should be noted that other configurations would require correction of measured H_2 volume.



Fig(1) Schematic diagram of the experimental set up for hydrogen evolution from endothermic reaction of citric acid with magnesium metal

Nano- graphene prepared in NRC lab. by modified Hummers method:

Modified Hummers method was used to prepare graphene oxide, where (15)gm $KMnO_4$ and (5)g graphene powder were put, in 500 ml. round bottom flask and stirred until homogeneous. A (9:1) mixture of sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) were sulfuric acid was added to homogeneous mixture. All system was placed in ice-water bath the reaction was heated to $50^\circ C$ with stirring 12h. Stirring continued until liquid paste was formed. The liquid paste was washed with distilled water until pH value was reduced down to 6. The filter cake was dried in vacuum oven at $80^\circ C$ for 48h.

Preparation of reduced graphene (RGO) by Exfoliation process:-

The dried graphite oxide was chemically exfoliated at $80^\circ C$ water bath for one hour. The suspension was subjected 15 min. to (540 rpm, 5 min. per cycle) yielding the final product.

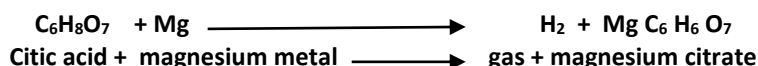
Preparation of ozonated modified graphene :-

A continuous flow of ozone gas $2\text{LO}_3/\text{min}$ flow rate in 200ml (KH_2PO_4 23.86 g/L solution) or double distilled water (DDW) was subjected to final (GO) product into ozone system [4].

TGA/TDA experimental settings by temperature scanning rate; $1\text{C}/\text{min}$; temperature range $20\text{ }^\circ\text{C}$ - $1000\text{ }^\circ\text{C}$ purging inert gas: N_2 .

Recovery of magnesium as pharmaceuticals after hydrogen evolution and reaction completion:

Magnesium metal and citric acid reacts to give hydrogen and salts as follows:



Recovery of magnesium as magnesium citrate which is used medicinally as:

- a-**Dietary** supplement (320 – 420 mg of elemental magnesium).
- b-A saline **laxative**(syrup of 1.745 g of magnesium citrate per fluid).
- c-**Food additive**(as a supplement in pill form, is useful for the prevention of kidney stones.)
- d- **Lowering for blood pressure**(Korean researchers evaluated and found participant with hypertension, those who take 300 mg of supplemental magnesium daily for three months had marked reduction in blood pressure.
- e- **Prevent Diabetes** (Swedish scientists studied magnesium benefits of diabetes and found for every 100 mg increase in daily intake of magnesium, there was a 15% decrease in type 2 diabetes).

3. RESULTS AND DISCUSSION

3.1 Evaluation of Hydrogen from Magnesium metal reaction with water and estimation of Energy:

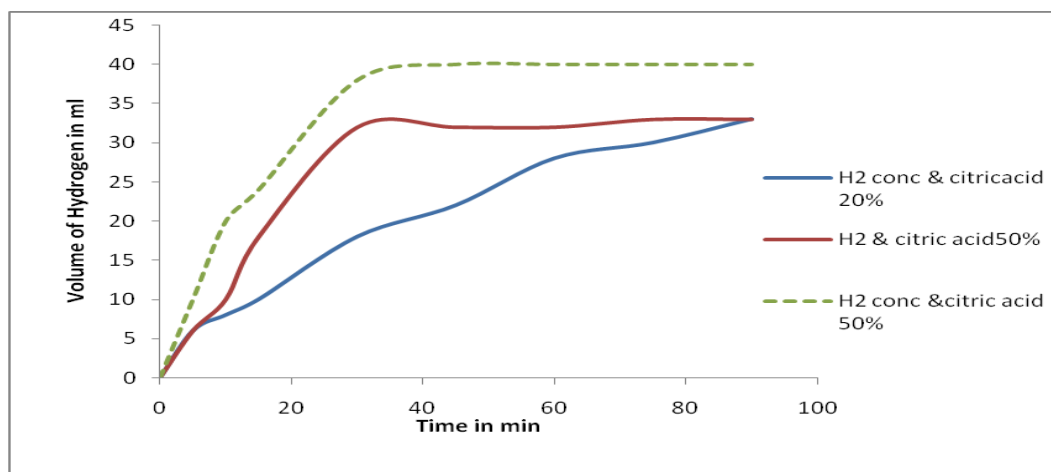


Fig (2) Effect of Citric acid concentration on Hydrogen generation

Fig (2) shows the endothermic reaction between citric acid and magnesium metal powder in tap water and in seawater at room temperature. The reaction curve shows the effect of different concentration ratios of citric acid with Magnesium metal on generated amount of hydrogen. The 20% solid citric acid dissolved in tap water shows slow evolution of hydrogen gas, gradually and regularly till reaction completion in 90 minutes. However, the 50% ratio citric acid dissolved in tap water, shows rapid evolution of hydrogen gas which reached its maxima and completion after 30 minutes at room temperature. Fortunately, nearly the same rapid trend was shown with 50% citric acid dissolved in seawater but with more increase in hydrogen generation by 20%. The reaction reached its completion after 30 minutes too. This increase in hydrogen generation is related to presence of other elements rather than added magnesium metal powder such as Al, Si, Ca, P, Br....etc. as shown in seawater content of Table(1).

Recovery of Magnesium after complete reaction as pharmaceuticals and as Magnesium Oxide:

Fig.(3) illustrates the EDX of magnesium citrate. Citric acid was preferable to hydrogen production by interaction of magnesium with its protons. Environmental safety of citric acid and its salts is important.

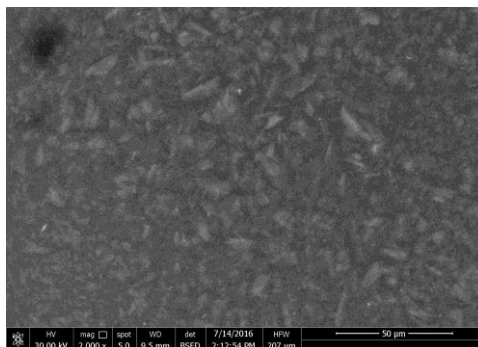
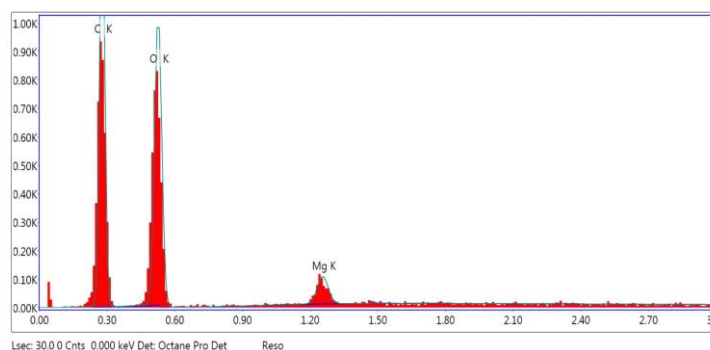


Fig (3)_a SEM morphology of dried magnesium citrate resulted from the hydrogen evolution reaction



Element	Weight %	Atomic %	Net Int.	Error %
C K	47.02	54.45	138.65	7.1
O K	51.29	44.58	134.38	10.5
MgK	1.69	0.97	18.65	12.15

Fig. (3)_b showing the EDX of the magnesium citrate formed after the Hydrogen evolution reaction

When magnesium citrate was calcined at 500 °C for two hours, the pure magnesium oxide crystals formed as shown in Fig.(4).

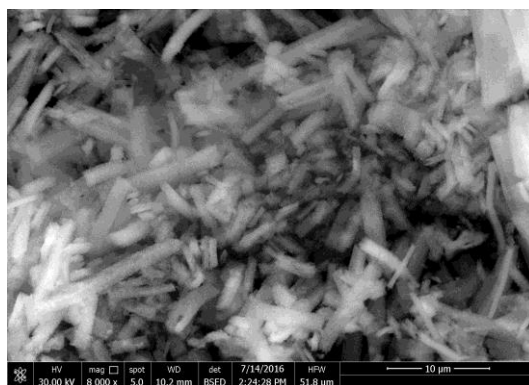


Fig. (4)a showing magnesium oxide crystals in orthorhombic rods

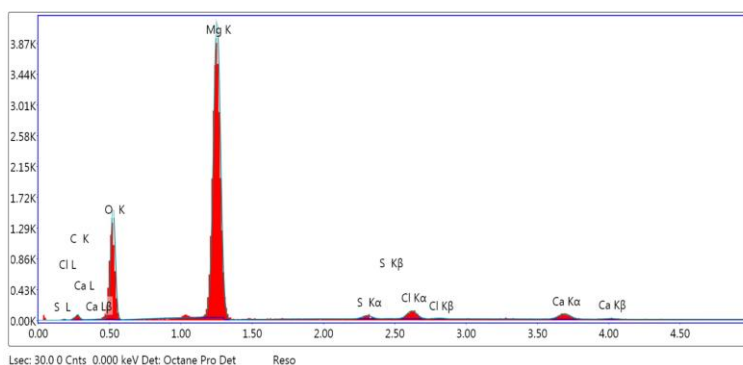


Fig (4)_b EDX chart of magnesium oxide produced by calcination of magnesium citrate at 500°C for two hours.

Element	Weight %	Atomic %	Net Int.	Error %
C K	6.48	10.49	6.87	19.37
O K	38.69	47.03	208.69	8.81
MgK	49.69	39.75	840.87	5.18
S K	0.78	0.48	11.8	20.51
ClK	2.17	1.19	31.74	12.4
CaK	2.19	1.06	25.67	13.98

Hydrogen storage in Nano-graphene and Nano-spun:

3.3.1 Graphene oxide was prepared by modified Hummer method and was then reduced by Exfoliation. The final product was modified by ozonation in presence of KH_2PO_4 and /or UV light. The TEM shows the morphology of modified graphene Fig. (5)_a Fig (5)_b-. XRD analyses shows the crystallite of modified graphene with UV light.

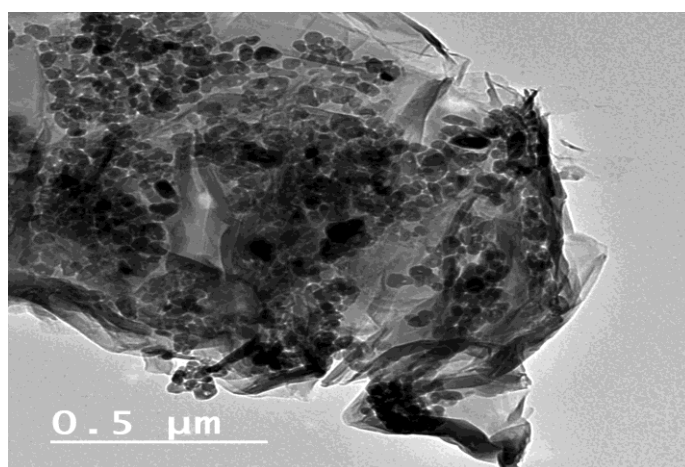
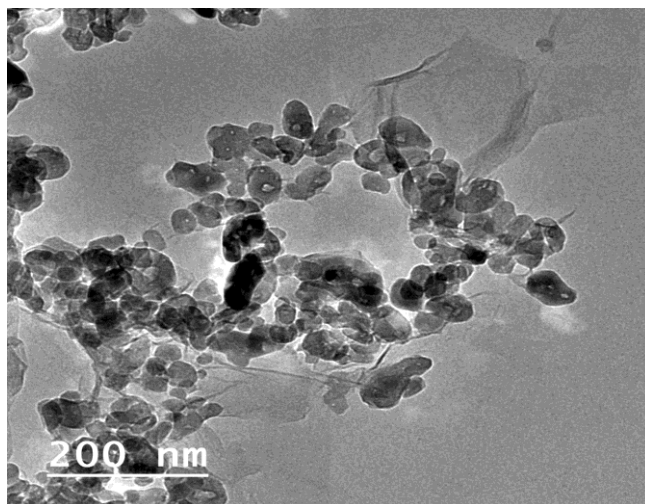


Fig. (5)a TEM Chart of Graphene (GO) treated with $2\text{LO}_3/\text{min}$ for 15 min in presence of $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ illustrating the hexagonal plane sheets.

TEM images revealed different morphologies. Analyses provided a wrinkles formed due to the overlap of the exfoliated GO layers induced. A rigid aggregate particles with a platelet like shape Fig(5)_b. Few curved tube-like graphene sheets are observed (dark-colored components) as a result of exfoliation process Fig(5)_b. Hydrogen adsorption depends on the nature/geometry and purity of the Nano-tube and high surface area porous carbons.

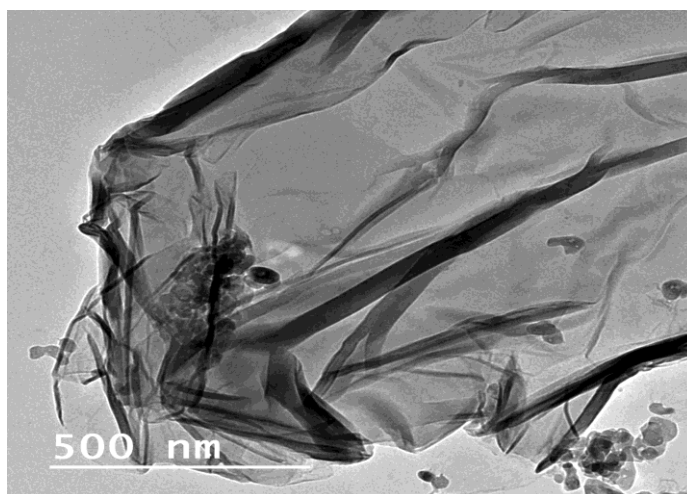


Fig. (5)b TEM Chart of Graphene (GO) treated with $2\text{LO}_3/\text{min}$ for 15 min in presence of $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$

Illustrating the curved tube-like graphene sheets.

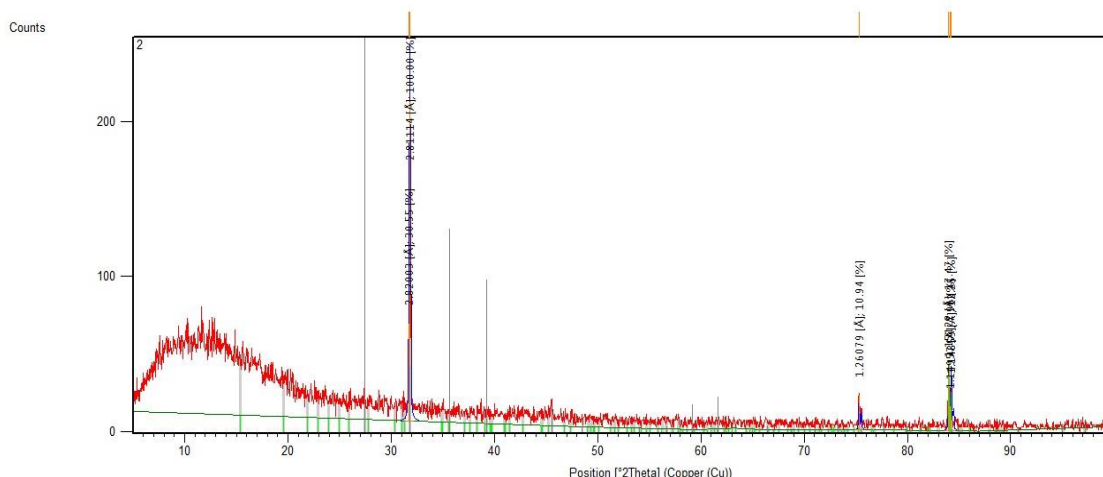


Fig (6) XRD chart showing the crystallite of modified graphene with ozone and UV light.

Stability of Graphene oxide studied by DSC/TGA:

DSC/TGA analysis for graphite, exfoliated graphene, and graphene oxide was studied as follows:

TGA curve shows decomposition of graphite before exfoliation Fig. (7) shows weight (loss 19.27%) at 208°C followed by significant weight (loss 79.22%) 215°C – 220°C due to pyrolysis of carbon skeleton.

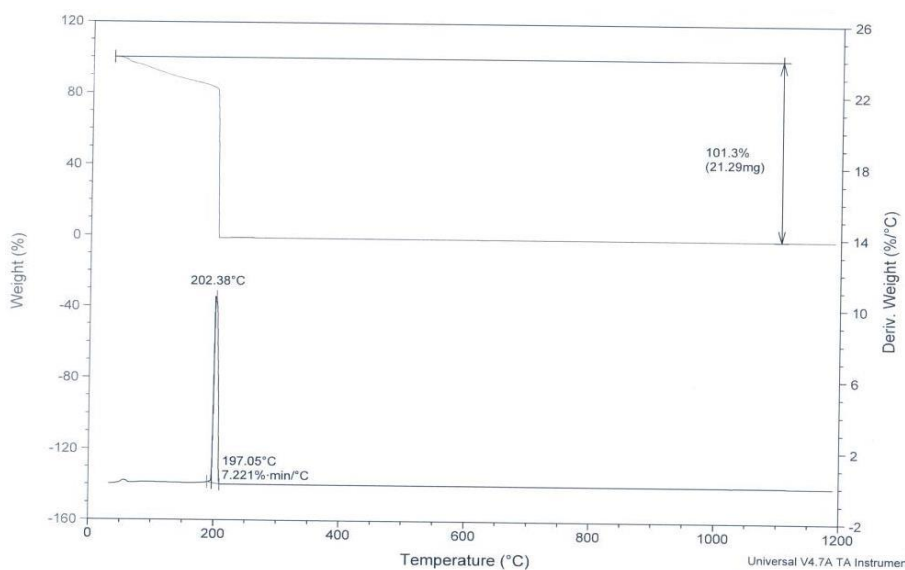


Fig (7) DSC/TGA curve of graphite before exfoliation

The DSC/TGA curve of ozonated graphene oxide Fig (8) illustrates three decomposition steps to weight loss during temperature increase. The first decomposition step appeared in temperature range 0°C - 190°C (loss 18.26%), near the boiling point of water. This is due to the loss of water absorbed from surface of (GO). The second decomposition step at 190 °C – 300 °C (loss 21.13%) results in the pyrolysis of attached oxygen functional groups. The third decomposition step appearing from 300 °C - 1000°C (loss 22.761%) is due to pyrolysis of carbon skeleton.

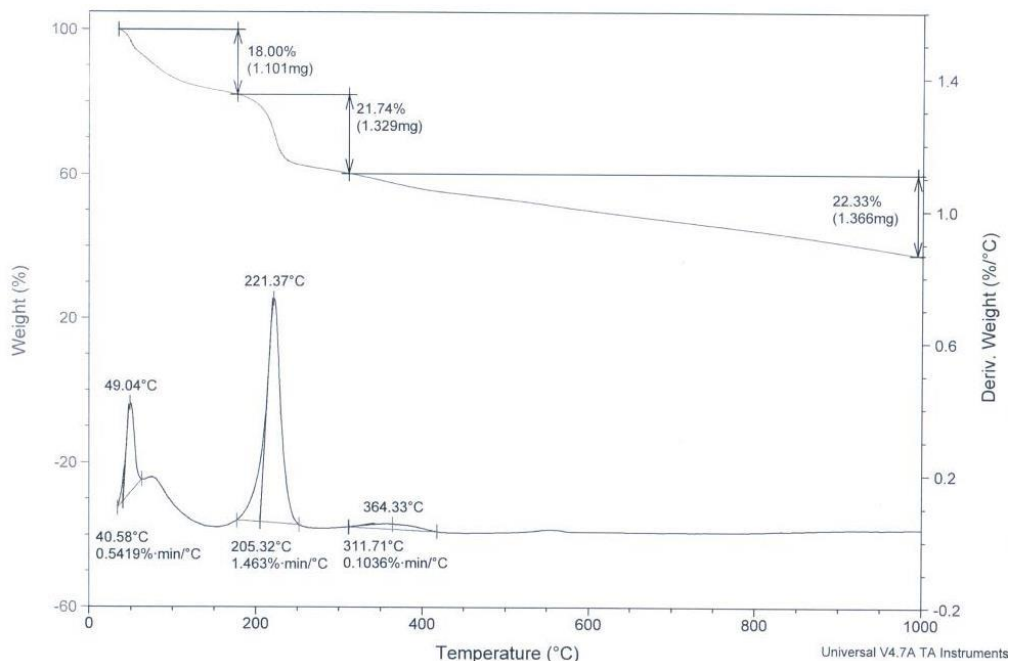


Fig (8) DSC/DGA curve of ozonated graphene oxide

Comparing the DSC /TGA curve of exfoliated graphene and without ozone modification, Fig.(9) showing a steady and loss from 0°C -202°C (loss 7.175%), indicating good reduction by using dipotassium hydrogen phosphate as reducing agent. A significant weight loss decomposition step appeared at 200°C- 1000°C (loss 99.98%) indicating pyrolysis of carbon skeleton.

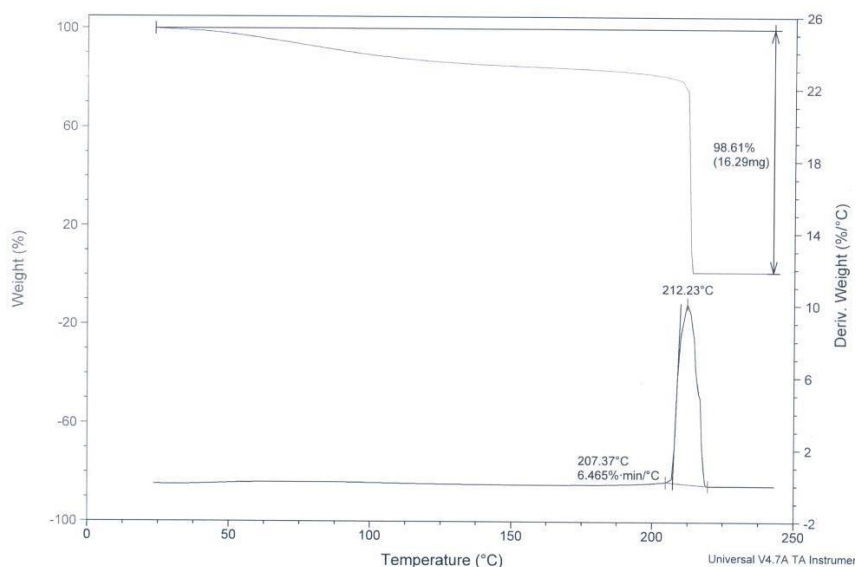


Fig (9) DSC/DGA curve of graphene oxide without ozonation

CONCLUSION

The hydrogen production in the reaction of magnesium metal with citric acid is economically profitable.

The reaction data shows that magnesium metal powder reached high value at completeness at normal temperature and can be a good energy carrier for hydrogen production.

Citric acid is weak, cheap and nontoxic acid which when added to magnesium water reaction markedly improve the volume and rate of hydrogen generation.

This technology, efficiently, safely, and without additives, minimize processing time and encourage recycling of magnesium as both pharmaceutical and as pure magnesium oxide.

Graphene **oxide showed** stability indicated by TGA curve. Mass loss at two temperature ranges 190°C and 300 °C are corresponding to oxygenated functional groups removal. Whereas the second step occurred around 600°C due to the bulk pyrolysis of carbon skeleton.

Carbon Nano-materials are excellent candidates for hydrogen storage, they results in slowing down of hydrogen absorption but increases reversible hydrogen storage capacity of material.

ACKNOWLEDGEMENTS

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Table (1) Main salts in Seawater used analyzed by XRF:

Main Constituents	Wt %
SiO ₂	0.74
Al ₂ O ₃	0.23
Fe ₂ O ₃	0.09
MgO	20.16
CaO	3.01
NaO	15.58
K ₂ O	3.09
P ₂ O ₅	0.06
SO ₃	9.67
Cl	46.89
Br	0.388
SrO	0.077

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