

Prospects of Sea Water Electrolysis for the Production of Hydrogen: An Exploratory Study on the Electrolysis of Magnesium Chloride Solution in the Presence of Sulfur

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Summary: It was hypothesized that the use of sulfur powder or sulfur electrode in the sea-water electrolysis would prevent (i) chlorine evolution, (ii) precipitation of Mg(OH)₂ and would at the same time result in the production of H₂SO₄, which might facilitate evolution of H₂. The hypothesis was tested with MgCl₂ solution as representative of sea water and using Pt, graphite, carbon felt working electrodes with sulfur powder and "sulfur" electrodes as working electrodes. Experimentally it was found that on the addition of sulfur or the use of a sulfur electrode (as anode), chlorine evolution was prevented on anode and Mg(OH)₂ precipitation was prevented on cathode and at the same time H₂SO₄ was produced. H₂ evolution, though confirmed, however, could not be quantitatively collected.

Prologue

The awareness of the limitation of Fossil fuel and the upheavals associated with it necessitates the desire to explore new sources of energy. It is appropriate to say that if the mankind is to survive, alternative energy sources must be found. It is, of course, advantageous, to tap those sources of energy which are renewable and / or clean and unlike fossil fuel, are not limited in quantity. One such energy source is hydrogen gas which can be produced from limitless and inexhaustible source – (sea) water. Water is regenerated from hydrogen.

Hydrogen as fuel [1-5] and production of hydrogen [6-10] are extensively studied subject matters. Enormous amount of references are available on web, however, the economy of hydrogen production is in question [11].

There are several methods for the production of hydrogen but sea-water electrolysis has its own charm – advantages as well as disadvantages. Electrolysis also requires energy. Electricity produced by windmills installed at a country's coastal area can provide cheap electricity [12-14]. However, the generation of electricity is not the purpose of this study.

Hydrogen gas can be produced from water by various means [6-10, 14-17]. These include photolysis, photo-electrolysis, electrolysis, chemical or thermal reformation of biomass *etc.* There are advantages and disadvantages of photo-chemical / photo electro-chemical methods, but again, in the present study, we are not interested in the merit / demerit of all these methods. Here, in the present

study, we are interested in some of the problem(s) in the electrolysis of sea and how to over-come them.

There are two major problems in the electrolysis of sea-water: (a) precipitation of magnesium hydroxide and calcium carbonate on the cathode [18] and (b) evolution of chlorine gas on anode [19, 20].

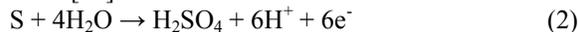
Instead of using actual sea water or complete artificial sea water, it was thought to better use magnesium chloride solution as a prototype substrate for the present exploratory study. In the electrolysis of MgCl₂, the same two problems are encountered (i) evolution of chlorine on anode and (ii) deposition of Mg(OH)₂ on cathode [18]. In some preliminary studies [20] there was an indication that the addition of sulfur prevented the evolution of Cl₂ and, at the same time, prevented the precipitation of magnesium hydroxide. These observations seemed worth pursuing further. Sulfur as sulfur powder, sulfur electrode, artificial charcoal with sulfur, epoxy-charcoal-sulfur, natural charcoal containing sulfur seemed suitable material to be tested for effectiveness.

Introduction

Water gets electro-oxidized at potential 1.23 V vs NHE

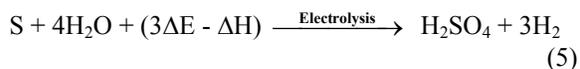
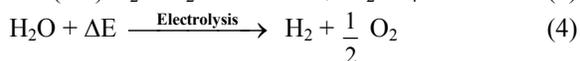
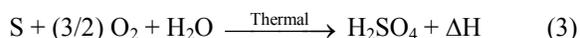


And sulfur gets electrolysed at 0.45 V vs NHE [17]



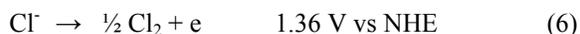
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It can be shown from the following relationships and thermodynamical reasoning that production of H₂, can be made rather favorable (eq.(5)) [21].



Since $\Delta\text{H} = -296.6$ kJ/mole and $E = 1.23\text{V}$ (vs NHE), which gives Gibbs free energy, from eq (5) as 206 kJ mole⁻¹ [21], which is smaller than required for eq (4) *i.e.* Sulfur might be oxidized electrochemically in water producing sulfuric acid and hydrogen and prevent O₂ evolution. The ease in production of hydrogen and sulfate ion in preference to oxygen evolution has been verified by Shih and Jong [21], whereas they used sulfur powder in the anodic compartment. There is no reason why some powdered mixture containing elemental sulfur can not be used for the same purpose. Why not to use a "sulfur electrode" [22-25].

The production of chlorine follows equation (6)



Experimentally in sea water electrolysis it is chlorine which starts evolving [26]. Bennett [27] discussed the competition between oxygen and chlorine evolution in the electrolysis of sea water. He concludes that as the electrolysis proceeds, chlorine evolution is favored over oxygen evolution. He prepared electrodes which could be used which favor oxygen evolution. Bennett also mentions the problem of Mg(OH)₂ precipitation in cathode compartment while electrolyzing sea water. The precipitation occurs due to change in pH (ranges 11-14) near the cathode as the reaction proceeds and Mg²⁺ is a major constituent of sea water (1200 ppm).

Bennett proposed a flow system to prevent clotting of the electrode because of Mg(OH)₂ precipitation.

Thus if sea water is electrolyzed with either sulfur powder in the anode compartment or with "sulfur electrode", then chlorine evolution may be prevented and according to eq (2), the generated H⁺ traveling to the cathode (compartment) will prevent Mg(OH)₂ precipitation, maintaining Ph < 7.0.

Thus the hypothesis would be tested: use of sulfur as powder or as anode will prevent Chlorine evolution as well as prevent Mg(OH)₂ precipitation. This to be done by electrolyzing MgCl₂ solution of the appropriate concentration using platinum, graphite, carbon felt electrodes, along with sulfur powder and / or sulfur electrode. Testing the product formation can be done (a) for the evolution of chlorine by the odor it imparts, (b) by visual inspection of the electrode surface for the deposition of Mg(OH)₂ and (c) for the formation of H₂SO₄, by testing the pH of the solution and testing for SO₄²⁻ by the reaction of electrolyzed solution with BaCl₂ for BaSO₄ precipitation. In the present study a dilute solution of MgCl₂ (0.01M) was used

Result and Discussion

Several electrolysis experiments were performed using two compartment and one compartment cells with various combinations of conditions and electrodes. Results are collected on Table-1.

It is noted that in the table no quantitative values are given. The purpose of this exploratory study was primarily to test the hypothesis that sulfur added to the electrolysis substrate (sea water, here MgCl₂ solution) would prevent

(a) precipitation of Mg(OH)₂, (b) evolution of Chlorine and would produce H₂SO₄ (and also produce hydrogen). Through this exploratory study it is demonstrated that sulfur either as powder or as artificial charcoal or as "sulfur electrode" does what the hypothesis claims about.

Whether a sulfur-containing natural charcoal can be de-sulfurized effectively in this way or not, it can not be concluded from this study. The epoxied-sulfurated charcoal gives what is assumed to be polysulfide(s). No analysis of this product was made. The problem of using sulfur powder is that on stirring, most sulfur powder tends to stay / float on the surface of solution. Thus an artificial/synthetic sulfur- charcoal or "sulfur electrode" is more efficient for the purpose: prevention of evolution of chlorine and precipitation of Mg(OH)₂. A two compartment cell seems logical to use. But sulfuric acid produced in the anode compartment takes more time to diffuse through a frit to the cathode compartment and in the mean time Mg(OH)₂ starts depositing on the cathode. Thus a one compartment cell is more efficient. The collection of H₂ gas remained an enigma. We believe due to leakages at various places in our electrolysis

cell, H₂ gas if collected, was very small in quantity (less than 0.2 cm³).

Experimental

Chemicals/Material

Magnesium chloride, sulfur powder, barium chloride, carbon (charcoal), hydrochloric acid, nitric acid – all Fisher Reagent Grade or Equivalent – were used. Deionized water was available in the laboratory. Natural charcoal containing unknown percent of sulfur was obtained from local market (Northridge, California, USA).

Sulfur was used as sulfur powder or as powdered-synthetic/artificial sulfur-charcoal or “epoxy” sulfur-Charcoal, or as “sulfur” electrode. These were fabricated as described later (see below).

Electrodes

Electrodes used were platinum wire, 2 cm length and 0.1cm radius; platinum foil 2.5 cm x 2.5 cm; platinum gauze 2.5 cm x 2.5 cm (50 mesh); graphite rod 10 cm long, 3mm radius, all obtained from AlfaAesar. Carbon felt was a gift from Department of Chemistry, Southampton University (U.K.), it can also be obtained from AlfaAesar.

Table-1^a: Electrolysis of Magnesium Chloride under various conditions.

S. No.	System	Electrode		Mg(OH) ₂	Cl ₂	SO ₄ ²⁻	pH (compartment)		H ₂ (d)
		Anode	Cathode				Cathode	Anode	
1.	MgCl ₂ 30 -100 mL (b)	Pt- Foil	carbon felt	+	+	-	> 8	2.5	+
			Potential =0.75V	Thick layer	V. Strong Odor				
2.	MgCl ₂ 30-100 mL + 0.5g S (powder) in anode compartment (b, c,f)	Carbon felt	Pt- Foil	+	+	+	< 8	2.5	+
			Potential V =0.75V Current I =9mamp	V. thin film	Strong Odor	BaSO ₄ Precipitation			
3.	MgCl ₂ 30 -100mL (b)	Pt- Gauze	Pt Foil	+	+	-	> 7	3	+
			V = 6.0V I = 3.8mamp						
4.	Mg Cl ₂ 30-100 mL + 1g S (powder) (b)	Pt- Gauze	Pt Foil	+		+	>7	3	+
			V = 4 V I = 0.75mamp	Thin film	V. faint Odor				
5.	MgCl ₂ 60 mL + 1 g S (powder) (c)	Pt- Gauze	Pt Foil	No	No	+	< 7	-	+
			V = 2.0V I = 6.0map						
6.	MgCl ₂ 60mL + 1 g S (powder) (c, g)	Pt- Gauze	Pt Foil	No	No	+	< 7	-	+
			V = 3.0V I = 15mamp						
7.	MgCl ₂ 60mL + Synthetic/artificial Charcoal (25% S) 1.0 g powder (c)	Pt Gauze	Graphite Rod	No	No	+	< 7	-	+
			V= 6.0V I= 10mamp - 20mamp						
8.	MgCl ₂ 60mL + 600mg epoxy Charcoal (25% S) powder (c)	Pt- Pt	Pt	-	No	-	□ 8	-	+
			V= 6.0V I= 8mamp (h)						
9.	MgCl ₂ 60mL + 2.00 g Natural Charcoal powdered, (untreated) (c)	(a) Pt- (b) Pt	Pt- C-felt	No	No		6	-	-
				No	No		6	-	(i)
			E= 6.0V I= 6.5map						
10	MgCl ₂ 60mL (c)	Pt- Gauze	Sulfur (C- felt)	No	No		6	-	+

(a) These results are representatives of 3-4 experiments done under the same conditions, most experiments were carried out for 10-12 hours and some time 2-3 days; electrolysis was carried out with two-electrode system. Generally vigorous stirring were carried out, Also, generally 1-2 drops of 1.2M HCl was added, (b) two compartment cell, (c) one compartment cell, (d) H₂ not collected, (e) carbon felt electrode was attacked by chlorine, (f) sulfur powder floats on the water surface, (g) acid not added, (h) some gluey black material formed at cathode, property of which not investigated., (i) hydrogen evolution not perceptible, less than 0.2 mL.

Sulfur Electrode

Sulfur electrode was fabricated either by quickly dipping a part of carbon felt (electrode) in molten sulfur under Argon; or dipping the felt in a sulfur-saturated solution of carbon disulfide.

Synthetic/Artificial Sulfur-Charcoal

Synthetic sulfur-charcoal (25% sulfur) was made by mixing 1.00 g pure sulfur and 3.00 g pure charcoal carbon and melting under Argon. After cooling, the lump was crushed and ground to fine powder.

Epoxy-charcoal (25% sulfur), 1.00 g sulfur and 3.00 g charcoal carbon were mixed and then blended with epoxy to bind them. After solidification (after 24-hours), the solid lump was crushed and ground to powder.

Equipment

Power Supply

Educational Instrument Model 2105. Digital Voltmeter / Multimeters. A "Pot" potentiometer for "regulated" power supply of desired power.

Electrolysis Cell

A Two compartment H-type cell was custom made and was similar to that of Shih and Jong's cell [21] (Fig. 1). A one compartment cell was also used.

The circuit was the usual one – the power supply as a source of stabilized d.c. power source; a "pot" potentiometer to regulate the desired power, resistor, multi-meters and the cell. These components were used in the circuit used for the purpose of electrolysis (Fig. 2).

In electrolysis generally 30 – 100 mL of solutions were used. 1-2 drops of 1.2M HCl was generally added to solution to initiate the electrolysis

Conclusion

Sulfur powder does stop the evolution of chlorine gas and precipitation of $Mg(OH)_2$ in the electrolysis of $MgCl_2$ (aq), most probably though the formation of sulfuric acid. It does not stop evolution of H_2 (g). Thus in sea-water electrolysis, for the production of H_2 (g), it may be more practical to use sulfur in the form of sulfur powder itself or as part of natural charcoal or "sulfur electrode".

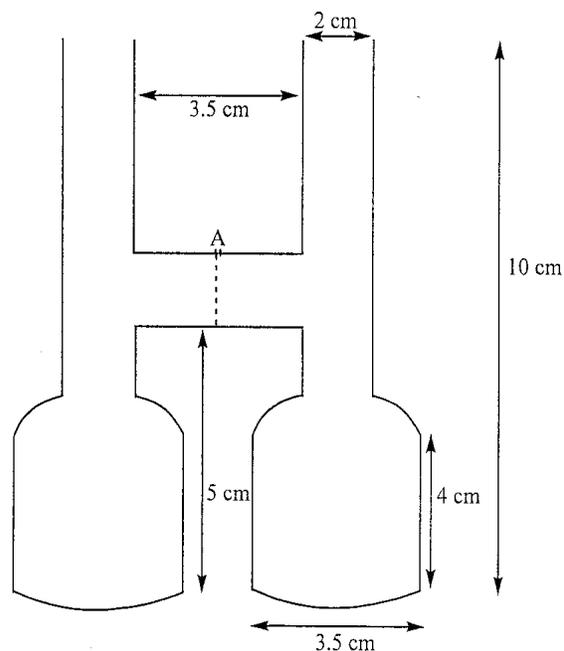


Fig. 1: Two compartment cell used for electrolysis.

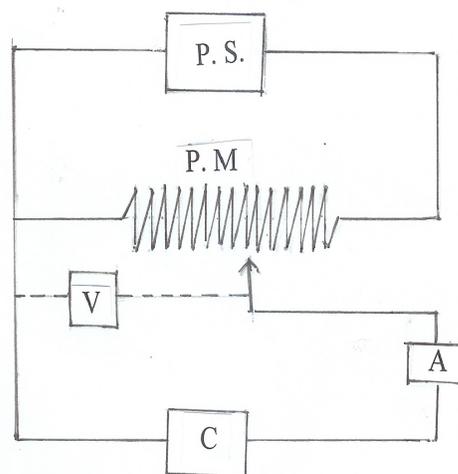


Fig. 2: The circuit diagram of the electrolysis setup: P.S = Power Supply, P. M. = potentiometer (voltage divider), V = Voltmeter, A = Ammeter, C = Electrolytic Cell.

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