



Hydrogen generation through cuprous chloride-hydrochloric acid electrolysis

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Abstract: Due to fast industrialization the consumption as well as the cost of fossil fuels like petrol, diesel etc in the world is rising enormously leading to the generation of greenhouse gases like carbon monoxide, carbon dioxide etc besides decreasing the availability of the above fuels. The emission of these greenhouse gases rises the globe's temperature leading the earth to face many dangerous complications. In order to save the earth from effect of rise of temperature and also to have an eco-friendly alternate energy fuel especially for the transport sector, attention is being focused on the generation of hydrogen gas which meets the above situations. During the combustion of hydrogen gas it emits only the beneficial water vapour to the atmosphere. In this research paper investigation has been carried out through CuCl-HCl electrolysis with 1M CuCl anolyte and 6M HCl catholyte for the generation of hydrogen gas at 70°C at normal atmospheric pressure employing a double compartment electrolytic cell having a nafion cation exchange membrane-324. Anode was graphite and cathode was 0.30 mg cm⁻² platinum coated graphite. At a current density of 250 A m⁻² the current efficiency for the oxidation of CuCl to CuCl₂ and the formation of hydrogen gas was nearly 100% and the rate of hydrogen liberation was found to be 2 l h⁻¹. Voltage efficiency and energy consumption values are calculated and are found to be more encouraging since they are more economical with less energy operation. The formed CuCl₂ was reduced back to CuCl anolyte by chemical reduction with copper powder in 6M HCl at 70°C and the regenerated CuCl anolyte was again used in the CuCl-HCl electrolysis.

Keywords: Cuprous Chloride-Hydrochloric Acid, Nafion Cation Exchange Membrane-324, Divided Cell, Graphite, Platinum Coated Graphite, Hydrogen Gas, Cupric Chloride

1. Introduction

The climate change is a very big challenge imposed on earth by the man mainly due to fast growing industrialization, automobiles, transport and fast developing electronic era. The outcome of this climate change that is global warming leads to various consequences like water pollution, air pollution, decrease in rice production, health, water scarcity in some area (less rain), copious water in some area (more rain) and so on. Warming of earth has been detected by scientists and they explain that it is due to the emission of green house gases like carbon dioxide, methane, nitrous oxide etc. Scientists have observed more acid content over the surface

of sea mainly due to the rain water having more acid levels. All these are primarily due to the over exploitation of usage of fossil fuels like coke, wood, petrol, diesel etc for producing electricity/meeting the fuel demand/energy requirement. Even then the energy demand could not be fully solved due to gradual decrease in their supply/production, increase of their price and also due to economic sanctions imposed on some countries having excess oil due to various political factors.

Due to the above consequences it is paramount necessity to have a substitute with clean renewable energy systems at competitive market costs with fast technological development. Rechargeable batteries store energy for latter

use can meet the energy demand only to a very little extent. The continuous use of storage batteries may generate solid and chemical wastes after their service life leading to various safe disposal problems. Among the promising energy substitutes the hydrogen gas has many attractive features like its multi functionality, cleanness, zero emission of green house gases only steam emission due to its combustion. Hydrogen is high in energy content as it contains 120.7 KJ g^{-1} .

Hydrogen gas can be produced from various sources besides from water which is abundant.

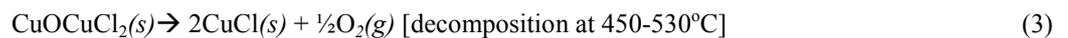
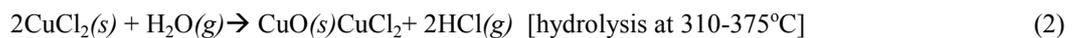
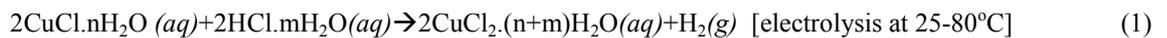
Hydrogen gas production from water by electrolysis is cited in [1,2,3]. Ref [4] furnishes the details of generation of hydrogen from the electrolysis of seawater. Liquid ammonia is another interesting source for the generation of hydrogen by electrolysis [5]. Hydrazine can also be used for the generation of hydrogen gas employing nanocatalysts [6]. Solar energy can be judiciously employed to produce hydrogen gas from water by electrolysis [7]. Biosynthesis route is also reported for producing hydrogen and ethanol from glycerol fermentation [8]. Steam Reforming is another way of producing hydrogen along with carbon dioxide capture [9]. Generation of hydrogen gas is also indicated through biocatalysed electrolysis [10].

Eventhough hydrogen can be produced through several routes as cited above these methods have many disadvantages due to the following factors like very expensive/high energy process, no guarantee for the availability of solar energy throughout the year, liberation of unwanted toxic gas like chlorine, conducting electrolysis with costly instruments like potentiostat besides dealing with highly corrosive liquid as electrolyte, involving costly chemicals like nanoparticles, very slow process like fermentation using costly organic chemical, liberation of greenhouse gases like carbon dioxide

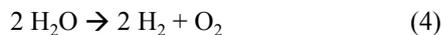
via steam reforming etc. But it is observed that hydrogen will not have a major role in India without considerable research on technology innovations and reductions in production cost. In that angle it is felt that hydrogen formation by a novel method other than cited above should satisfy these criteria. Hydrogen formation through the thermochemical cycles is an example for this. Thermochemical cycles combine solely heat sources like steam, nuclear and thermal heat with chemical reactions to split water into hydrogen and oxygen. The word cycle is used since water is split into hydrogen and oxygen while the chemicals employed in these processes are continuously recycled. Eventhough there are many thermochemical cycles available before us like cerium-chlorine [11], iron-chlorine [11], copper-sulphate [11], vanadium-chlorine [12], magnesium-iodine [13] and sulphur-iodine [14] the copper-chlorine thermochemical cycle is found to be best since it has a very low operating temperature of less than 550°C than other thermochemical cycles.

The optimised copper-chlorine (Cu-Cl cycle) is a three-step thermochemical cycle for generating hydrogen gas. The Cu-Cl cycle is a hybrid process involving both thermochemical and electrolysis steps. Its maximum operating temperature is about 530°C . This cycle involves four chemical reactions for the splitting of water whose net reaction is the decomposition of water into hydrogen and oxygen. All other chemicals that are involved are recycled. To attain maximum efficiency, minimum environmental impact and minimum cost of hydrogen generation the Cu-Cl cycle can be joined with waste heat available from solar, industry and nuclear plants. The Cu-Cl cycle is one of the prominent thermochemical cycles under development within the Generation IV Internal Forum (GIF).

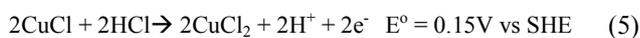
The reactions in the Cu-Cl cycle are given below [15,16].



Net reaction is the splitting of water into hydrogen and oxygen gases as shown by the equation given below.



In reference to the reaction (1) the principle of CuCl-HCl electrolysis is that cuprous chloride, CuCl which is dissolved in high concentrated HCl is employed as anolyte (electrolyte surrounding the anode) while high concentrated HCl is used as catholyte (electrolyte surrounding the cathode) in an polyethylene made electrolytic divided closed cell employing cation exchange membrane. The CuCl in HCl is present as chloride complexes like CuCl_2^{1-} and CuCl_3^{2-} when the HCl concentration is around 6M. As shown by Eq (1) when the DC current is applied to the cell the cuprous chloride (CuCl) anolyte is oxidized to cupric chloride (CuCl_2) as given below.



The catholyte (HCl) is reduced to hydrogen gas as

indicated below.



This research paper presents the result generated on the formation of hydrogen gas with minimum cell potential from the electrolysis of acidic cuprous chloride-hydrochloric acid system employing a divided electrolytic closed cell having cation exchange membrane using graphite anode and platinum coated graphite cathode under various experimental conditions.

2. Experimental

2.1. Cell for Basic Studies Using Cyclic Voltammetry

A three electrode glass cell with volume capacity of 150 ml with Pt foil as working electrode, Pt rod as counter electrode and Ag-AgCl as reference electrode was employed

for undertaking basic studies with Autolab system. All experiments were carried out at room temperature and potentials were measured. Before each cyclic voltammetric (CV) study, the working electrode was polished by fine emery paper followed by cleaning and washing. All electrode potentials other than CV in this research paper are given in respect of saturated calomel electrode (SCE).

2.2. Electrolytic Cell for Applied Studies

Fig 1 depicts the cell set-up for the generation of hydrogen gas with the formation of cupric chloride from the CuCl-HCl electrolysis.

A filter press type closed divided cell made up of polypropylene material for high temperature operation was fabricated employing graphite plate anode and platinum coated graphite plate cathode. The electrolytes, anolyte (CuCl in 6M

HCl) and catholyte (HCl) were circulated in the electrolytic cell through peristaltic pumps at moderate flow rates. The electrolytic solutions taken in the round bottom flasks were heated externally by heating mantles. Nafion cation exchange membrane was used as membrane in the cell. Provisions were made in the cell for measuring the electrode potentials during the electrolysis with saturated calomel electrode as reference electrode and also having provision for measuring the temperature in each compartment. Tygon tube which can withstand high operating temperature and high acid concentration was used in the cell set-up for the circulation of electrolytes. Cell having about 1 l volume capacity with 5A current was fabricated in our lab (CECRI, Karaikudi) and used in the experimental investigations of CuCl-HCl electrolysis for the formation of cupric chloride and generation of hydrogen gas with high efficiency and high purity.

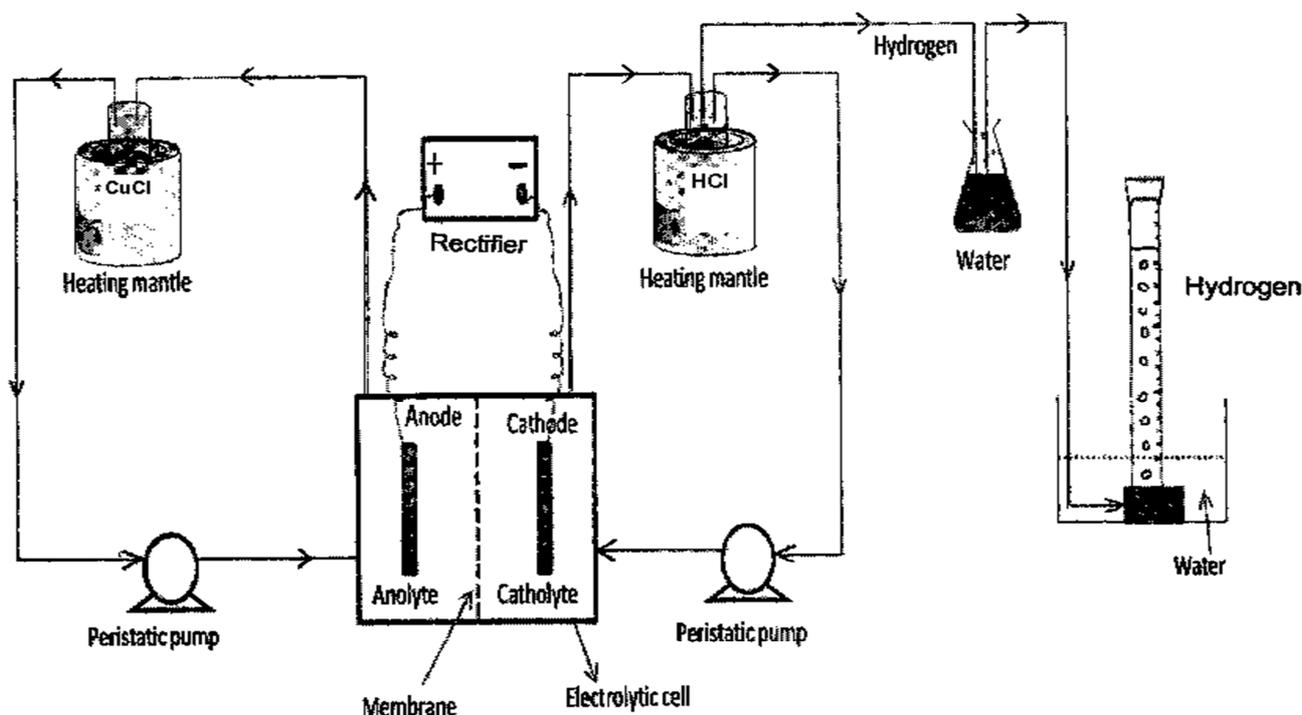


Fig 1. Cell Set-Up for the hydrogen generation through CuCl-HCl electrolysis

The galvanostatic experimental studies were conducted in a divided closed double compartment cell capable of holding 400ml of electrolyte in each compartment separated by nafion cation exchange membrane-324. The cell consisted of PP (polypropylene) frames of size 22cm length x 15cm breadth x 1.25cm thick for the cell with provision for the inlet and outlet in each compartment which functioned as anolyte and catholyte compartments. Graphite plates of the same size were used as anode and cathode (with Pt coating of $0.1-0.5 \text{ mg cm}^{-2}$). Anolyte (CuCl in 6M HCl, $1100 \text{ ml at } 40 \text{ l h}^{-1}$) and catholyte (HCl, $1100 \text{ ml at } 10 \text{ l h}^{-1}$) were circulated by peristaltic pumps through tygon tubes into the respective compartments from the reservoirs (multi neck round bottom glass flask) of 2 l capacity. The electrolyte solutions were heated to the required temperatures ($30-85^\circ\text{C}$) through heating mantles separately. Electrolysis was conducted for a

period of 1-5 h in the range of current density of $250-1000 \text{ A m}^{-2}$ with a minimum inter electrode gap of 1.5 cm. The liberated hydrogen gas from the cathode chamber is passed through the distilled water kept in a sealed glass conical flask and then the hydrogen gas was allowed to pass through a trough having inverted glass measuring jar to collect the purified hydrogen gas besides measuring the volume of hydrogen gas.

2.3. Characterization of Graphite Electrodes

Scanning electron microscopy (SEM) has been used for studying and characterizing the surface morphology of plain graphite cathode, Pt coated graphite cathode before and after electrolysis.

3. Results and Discussion

3.1. Basic Studies with Cyclic Voltammetry

The net electrolytic reaction taking place in the Cu-Cl electrolysis is



Basic study was carried out using CV for understanding the reaction mechanisms and also for knowing electrode potentials in the CuCl-HCl electrolysis for the generation of hydrogen gas. CV was carried out with HCl with the range of 1-11M for determining the potential for hydrogen liberation in the potential range of 0.00V to -1.00V with potential scan of 100 mV s⁻¹ with Pt wire as working electrode and Pt rod as counter electrode. The potential was found to be less negative from -0.38V to -0.14V as the HCl concentration was increased from 1M to 11M. In Fig 2 a cathode potential of -0.18V was observed for the hydrogen liberation from 6M HCl.

This is in conformity with the literature [17] since at this concentration of 6M HCl the precipitation of CuCl is avoided besides having observed less potential for the hydrogen liberation.

The CV of CuCl solution is shown in Fig 3. CuCl solution with 0.08M strength was prepared in 6M HCl for the potential measurements in the potential range of 0.00V to +0.75V having a scan rate of 50 mV s⁻¹.

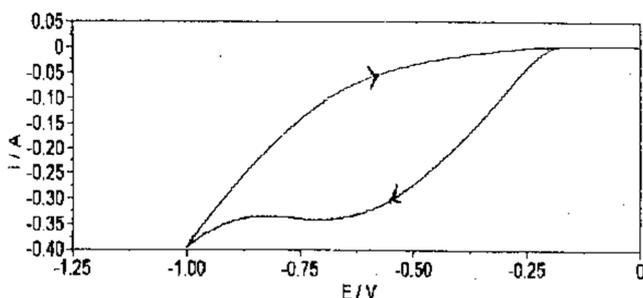


Fig 2. Cyclic Voltammogram of 6M HCl: 0.5mm dia Pt wire working electrode, 2mm dia Pt rod counter electrode

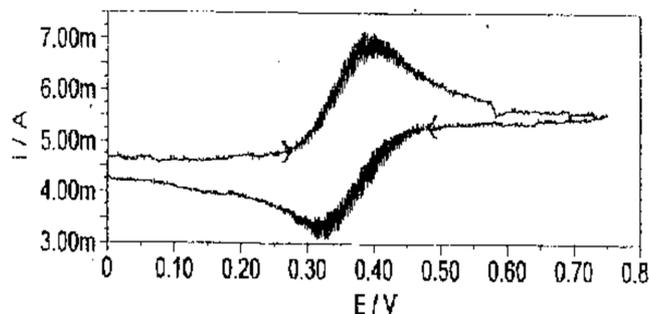


Fig 3. Cyclic voltammogram of 0.08M CuCl: 0.5mm dia Pt wire working electrode, 2mm dia Pt rod counter electrode

One anodic peak E_{a1} (Cu^{1+} to Cu^{2+}) at 0.400V and one cathodic peak E_{c1} (Cu^{2+} to Cu^{1+}) at 0.325V was observed. During the CuCl-HCl electrolysis since the cell voltage observed was less than 1V, practically no chlorine evolution

was observed in the anolyte (CuCl) compartment. Only cupric chloride is formed due to the oxidation of CuCl in the anolyte.

The formed cupric chloride is chemically completely reduced back to cuprous chloride by treatment with 10% excess stoichiometric amount of copper powder in presence of 6M HCl at 70°C under stirring for 30 min. The regenerated CuCl is again used in the CuCl-HCl electrolysis.

Since platinum is a very costly metal, experiments were carried with cathodes of graphite and Pt metal coated (0.30 mg cm⁻²) graphite for the potential measurements of hydrogen liberation from 6M HCl solution. The potential was -0.78V for plain graphite electrode, -0.39V for the Pt coated graphite electrode and -0.18V for Pt electrode. Considering the economic cost factor of Pt metal, Pt coated graphite electrode was subsequently used for all applied work since the rise in potential for the hydrogen liberation potential was only about 0.20V and the stability of Pt coated graphite was found to be very high in the CuCl-HCl electrolysis upto a duration of 50 h.

3.2. Applied Studies of CuCl-HCl Electrolysis

The galvanostatic CuCl-HCl electrolytic studies conducted is shown in Fig 1. During the electrolysis a cell voltage of 2.00V was observed at room temperature. Hence various investigations were carried out with the sole aim of decreasing the cell voltage/energy.

The various parameters like temperature, anolyte concentration, catholyte concentration, cathodic current density and Pt coated graphite cathode play very crucial role in the CuCl-HCl electrolysis for generating hydrogen gas from catholyte and cupric chloride from anolyte with minimum electrode potential/energy. In order to achieve minimum cell voltage, the above parameters were investigated on CuCl-HCl electrolysis and the results are discussed below.

3.3. Effect of Temperature

High temperature electrolysis is more efficient economically than traditional room-temperature electrolysis because some of the energy is supplied as heat, which is cheaper than electricity, and also because the electrolysis reaction is more efficient at higher temperatures. At higher temperature, the particles have more kinetic energy. They move more rapidly through the solution, they collide more often and more vigorously, so the chance of a reaction increases. The time taken for a certain amount of collisions to occur decreases, so the overall time for the reaction to occur would also decrease. As given in [18] high temperature electrolysis reduces the cell voltage.

The effect of temperature with a range from 30°C to 85°C was investigated on the CuCl-HCl electrolysis for the formation of cupric chloride and the generation of hydrogen gas. The cell voltage decreases with increase of temperature and after 70°C the decrease is only marginal and hence 70°C is fixed as optimum temperature for the specified conditions.

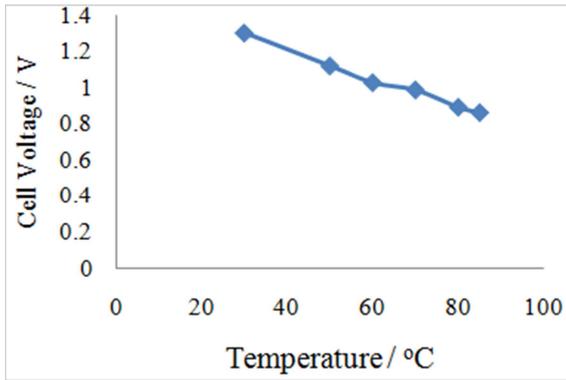
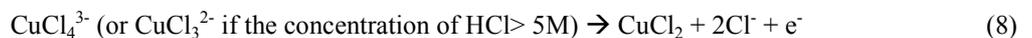


Fig 4. Effect of temperature on CuCl-HCl electrolysis with 1M CuCl+6M HCl anolyte, 6M HCl catholyte, 250 A m⁻² CCD; 5 h, 0.30 mg cm⁻² Pt coated graphite cathode

The result of this investigation is presented in Fig 4 shown above. In this study the diffusion of copper from the anolyte into catholyte was found to be only 0.30 g l⁻¹ of copper. Platinum coated graphite was employed as cathode material and graphite plate as anode. In all these experiments the hydrogen gas liberation efficiency was found to be ~ 100%. Eventhough further increase in temperature decreased the cell voltage marginally, due to operational difficulties experiments could not be carried out at temperature greater than 70°C.

3.4. Effect of Anolyte Concentration

With the aim of reducing the anode potential on the oxidation of Cu¹⁺ into Cu²⁺ at the graphite anode the CuCl-HCl electrolysis was carried out with varying cuprous



This reaction could occur if the free chloride (HCl) ion concentration is above 4M. The reaction at the cathode is



Fig. 6 describes the reduction of protons to form hydrogen gas.

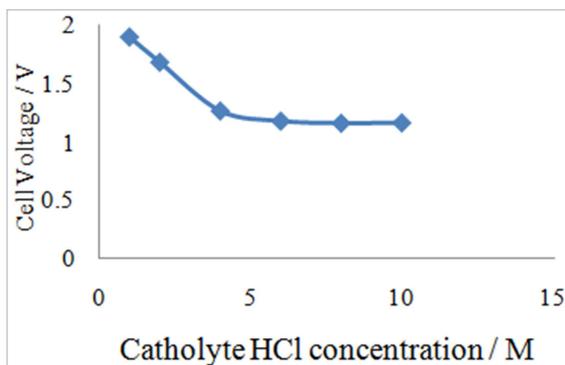


Fig 6. Effect of catholyte concentration of CuCl-HCl electrolysis with 1M CuCl+6M HCl anolyte, 500 A m⁻² CCD, 2.5 A, 2 h, HCl catholyte

The advantage of increasing HCl concentration is that the amount of Cu diffusion into the cathode compartment could

chloride concentrations (anolyte) in the range of 0.17 to 1.5M and it is shown in Fig 5.

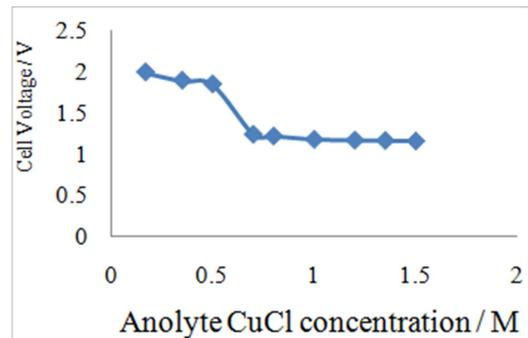


Fig 5. Effect of anolyte concentration in CuCl-HCl electrolysis with 6M HCl catholyte, 250 A m⁻² CCD, 1.25 A, 2 h, CuCl in 6M HCl anolyte

For the graphite anode the increase of cupric chloride formation with cuprous chloride concentration was obvious. At 1M CuCl concentration the CuCl₂ formation leveled off. The cell voltage was diminished by increasing the cuprous chloride concentration and after the 1M level the decrease in cell voltage was only meager. It is a common fact [19] that the use of high concentration of asolution is always recommended for an industrial production of its oxidized product. The studies were carried out at room temperature at a current density of 250 A m⁻² in a closed divided perspex cell.

3.5. Effect of Catholyte Concentration

This is shown in Fig 6. In [20], the anode side of electrolysis cell, Cu¹⁺ is oxidized to Cu²⁺ as

be minimized besides the reduction in the cell voltage.

For determining the optimum hydrochloric acid (catholyte) concentration, CuCl-HCl electrolysis was carried out in the perspex divided closed cell at room temperature with 1M CuCl+6M HCl anolyte with catholyte concentrations in the range of 1-10M HCl and the result is presented in Fig 6 shown above. From the result, 6M HCl was found to be optimum concentration. At lower HCl concentration (<4M) thin film of Cu over cathode surface was noticed, but at 6M HCl there was hardly a film of copper on the cathode.

3.6. Effect of Cathodic Current Density

The effect of cathodic current density, CCD, in the range of 250 – 1000 A m⁻² shown in Fig 7 was investigated at room temperature keeping the anodic current density (ACD) at 250 A m⁻².

The minimum CCD that could operate the electrolytic cell was found to be 250 A m⁻². With rise in CCD, the cell voltage marginally increased and the 250 A m⁻² CCD gives the minimum cell voltage. With 0.30 mg cm⁻² Pt coated graphite cathode, the rate of proton reduction into hydrogen rose almost linearly with the CCD with the indication on the corresponding increase on cell voltage. A higher cell voltage

of 1.882V was observed for the high CCD of 1000 A m⁻². The CCD could not be increased further than 1000 A m⁻² due to the onset of the copper deposit film over the platinum coated graphite cathode. Hence the optimum CCD was arrived at 250 A m⁻². This result was in conformity with the chloride production from aqueous chloride solutions [21]. The observance of increased cell voltage due to increasing current density is matching with ref [18].

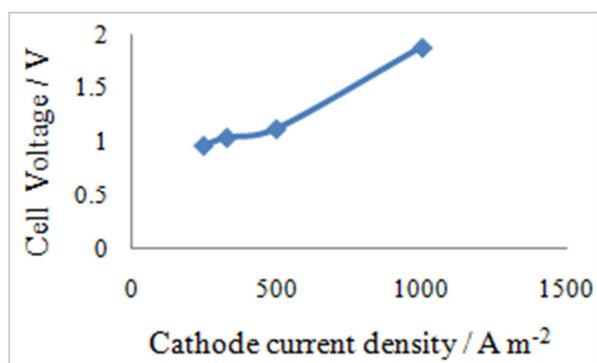


Fig 7. Effect of cathode current density on CuCl-HCl electrolysis at 5 A, 5 h, 1M CuCl+6M HCl anolyte, 6M HCl catholyte

3.7. Effect of Platinum Coated Graphite Cathode

The choice of electrode materials can greatly impact the electrochemical kinetics. From the literature, it is known that the reaction rate for Cu¹⁺ oxidation is roughly three times speedier on a platinum electrode (anode) when compared to a carbon surface electrode like graphite [22]. When such electrodes surface area is increased due to coating materials over them there is a scope for some reduction in their electrode potentials.

Since plain graphite cathode gave high cathode potential, it was coated with Pt with varying concentrations and its optimum level was determined on the CuCl-HCl electrolysis at 70°C. The range of platinum concentration coated over the graphite cathode is 0.1 - 0.7 mg cm⁻². Fig 8 gives the experimental results obtained on this study.

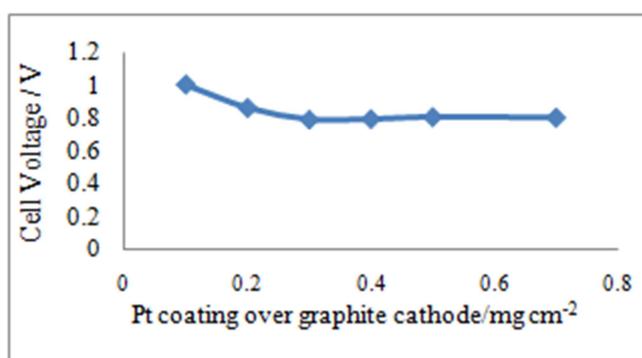
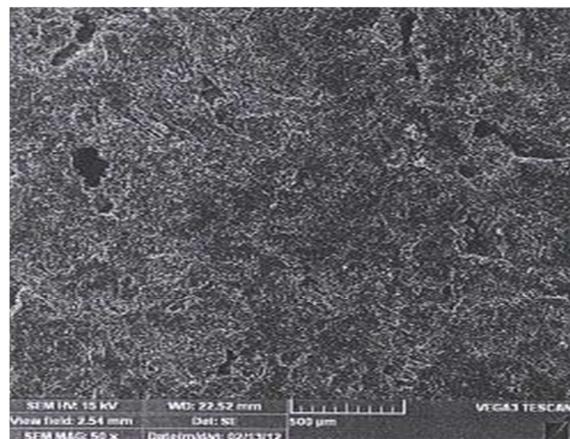


Fig 8. Effect of Platinum coating over graphite cathode in CuCl-HCl electrolysis with 1M CuCl+6M HCl anolyte, 6M HCl catholyte, 0.75 A, 2 h

From the figure, it could be seen that 0.30mg cm⁻² coating level of platinum is found to be optimum since it gives low cell voltage and beyond this level there is hardly any appreciable reduction in cell voltage value.

3.8. Characterization of Graphite Cathode

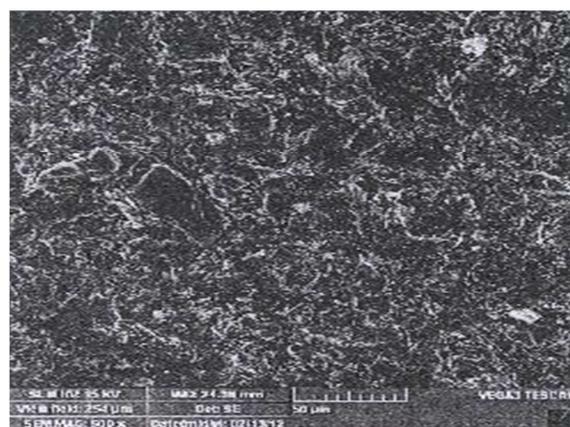
The scanning electron microscopy (SEM) taken for plain graphite cathode and 0.30 mg cm⁻² Pt coated graphite cathode both before and after CuCl-HCl electrolysis are given in Fig 9(a-c).



(a)



(b)



(c)

Fig 9. (a) SEM of plain graphite cathode, (b) SEM of Pt coated graphite cathode before CuCl-HCl electrolysis, (c) SEM of Pt coated graphite cathode after CuCl-HCl electrolysis with 5A, 5h, 1M CuCl+6M HCl anolyte, 6M HCl catholyte

The SEM for plain graphite cathode before electrolysis

given in Fig 9a shows a non-uniform electrode surface having many holes while Fig 9b indicates its surface gets uniform grain size when it is coated with Pt before electrolysis. Fig 9c presents the surface level of Pt coated graphite cathode at the end of electrolysis which does not have any hole but showing the presence of Pt even after the liberation of hydrogen gas indicating the good adherence of Pt coating over the graphite surface.

3.9. Calculation of Voltage Efficiency

The voltage efficiency of electrolysis is the ratio of theoretical cell voltage to the actual cell voltage. In the CuCl-HCl electrolysis the current efficiency of CuCl into CuCl₂ (anodic reaction) and 2H⁺ into H₂ (cathodic reaction) are ~ 100%. Theoretical cell voltage is: 0.230V (anode potential) - (-0.240V cathode potential) = 0.470V. The actual cell voltage is: (0.370V) anode potential - (-0.330V) cathode potential + (0.100V) membrane drop = 0.800V. Hence the voltage efficiency is 0.470 X 100/0.800 is 58.75% which is found to be economical.

3.9.1. Calculation of Energy Consumption

Under the optimum conditions, the CuCl-HCl electrolysis cell is run for 5 h at 5 A current giving an average cell voltage of 0.80V liberating 10.4 l of hydrogen gas (0.928g) and formation of 59.3 g of CuCl₂ (at 70°C, normal atmosphere).

Energy consumption, EC (for hydrogen generation at cathode compartment)

$$= CV \times \text{current} \times \text{duration} = \text{EC in Watt Hr}$$

$$= 0.80 \times 5 \times 5 = 20 \text{ Watt Hr}$$

= 20 x 1000 = 20000 Kilo Watt Hr (for generating 10.4 l of H₂ gas ie., 0.928g of H₂ gas)

$$= 20000 / 0.928 = 18560 \text{ Watt Hr (for generating 1.000g of H}_2 \text{ gas)}$$

= 18560 / 1000 = 18.56 Kilowatt Hr/Kg of H₂ gas

Energy consumption, EC (for cupric chloride formation at anode compartment)

$$= CV \times \text{current} \times \text{duration} = \text{EC in Watt Hr}$$

$$= 0.80 \times 5 \times 5 = 20 \text{ Watt Hr}$$

= 20 x 1000 = 20000 Kilo Watt Hr (for the formation of 59.3g of CuCl₂)

$$= 20000 / 59.3 = 337.2 \text{ Watt Hr (for forming 1.000g of CuCl}_2 \text{)}$$

$$= 337.2 / 1000 = 0.337 \text{ Kilowatt Hr/Kg of CuCl}_2$$

The energy consumption values of hydrogen gas generation and CuCl₂ formation are found to be very less leading to more energy savings.

4. Conclusions

The combustion of fossil fuels like diesel, petrol emits dangerous greenhouse gases leading to various detrimental effect on soil, water and air besides warming the globe. In this research study in order to avoid the above consequences hydrogen gas was generated through electrolysis of CuCl-HCl in a nafion cation exchange membrane-324 divided closed cell made of polyethylene material for withstanding

high temperature of 70°C at normal atmospheric pressure based on Cu-Cl thermochemical cycle with plain graphite anode and 0.30 mg cm⁻² platinum coated graphite cathode. During the electrolysis 6M HCl was employed as catholyte while 1M CuCl having 6M HCl was used as anolyte with the anolyte circulation at 40 l h⁻¹ and catholyte circulation at 10 l h⁻¹. The electrolysis was carried out at 250 A m⁻² cathode current density having tygon tubes for bath careers for a duration of 5 h. Cuprous chloride is oxidized to cupric chloride with 100% current efficiency and hydrogen gas was generated with 100% current efficiency with high purity at the rate of 2 l h⁻¹ in the specified cell conditions. This study has demonstrated that hydrogen gas could be generated with minimum energy having the average cell voltage of 0.78V. The voltage efficiency and energy consumption values of this electrolysis are found to be more promising since the CuCl-HCl electrolysis can be operated with less energy for the production of hydrogen gas.

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