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Electrochemical splitting of water on IrO_2 based Nafion bonded composite anode for efficient production of low cost and clean hydrogen fuel

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Hydrogen gas of ultrapure form has been produced via electrochemical splitting of water molecules using an efficient water electrolysis method. The IrO_2 based low-cost composite anode has been developed in the laboratory to split water molecules via electrolysis with the cathode electrocatalyst as Pt (40 % by wt.)/C_{HSA}. The electrocatalysts loading at anode and cathode are 1 mg/cm^2 at both electrodes. Other components of the manufactured electrodes are Nafion® (5 wt%) ionomer dispersion, PTFE, and isopropyl alcohol. The electrolyzer is fabricated using a perspex sheet i.e., polymethyl methacrylate. The rate of hydrogen production is measured for different applied currents, voltage, and concentrations of H_2SO_4 electrolyte in the electrolysis mode at a temperature of 20 °C. The IrO_2 composites anode used as oxygen evolution reaction are studied by electrochemical impedance studies (EIS) and cyclic voltammetry to evaluate the electrocatalytic activity and charge transfer resistance of the developed composite anode. The IrO_2 anode electrode exhibits a higher HER activity concentration of 0.75 M H_2SO_4 electrolyte than that of the 0.25 M and 0.50 M H_2SO_4 electrolyte concentration as is shown by EIS. The highest hydrogen production rate of 0.9 mL/min is obtained at the voltage of 1.9 V and applied current of 0.1 A using the electrolyte concentration of 0.75 M H_2SO_4. However, the hydrogen production rate is very low (0.33 mL/min.) when a low voltage of 1.6 V and current of 0.04 A was applied at the same concentration of electrolyte (0.75 M) H_2SO_4. IrO_2 is known to be one of the most active electrocatalysts for the oxygen evolution reaction in a liquid electrolyte, exhibiting high electronic conductivity and stability in the electrochemical system.

Keywords: Clean Hydrogen, Composite anode, Electrochemical water splitting, Environmental pollution

Introduction

The environmental pollution problem is a major problem of the modern world. The development of any country depends upon its energy resources and proper utilization. Currently, fossil fuel is the major energy resource (coal, natural gas, and petroleum) which can harm seriously the ecosystem by producing greenhouse gases[1]. These problems enforce the world to look upon alternative clean energy technology and resources. Hydrogen is the fuel most often used in fuel cells for electrical energy production apart from fuel cell, there are many other devices where hydrogen is used as fuel for power generation like internal combustion engines of automobiles and power generators [2,3]. Hydrogen is also used as raw materials for many products manufacturing like NH_3, urea, petrochemicals, etc. It can have many production routes like electrolysis of water, cracking, or reforming of petroleum products. The production rate of hydrogen and its degree of purity depends on the choice of catalyst, electrolyte, and operating conditions. The hydrogen production by the water electrolysis method is very interesting and useful because it is a pollution-free, very simple process, and renewable with a high degree of purity[4]. In addition, it remains as the basic technique for providing applications that require small volumes of high purity hydrogen, including the semiconductor and food industry. Hydrogen is the simplest of all known chemical elements. Although, this gas does not exist in its natural state as H_2, it is found in many molecules like water, sugar, proteins, hydrocarbons, and so on. Hydrogen is a very light gas, colorless, odorless, extremely inflammable, and reacts very easily in the presence of other chemicals. The properties of hydrogen gas are non-polar, its solubility in water is very small, its melting point is 13.8 K and boiling point is 20.4 K which are quite low[4]. The advantages of using hydrogen as a fuel are high due to high electrochemical reactivity, high theoretical energy density and its harmless combustion product (H_2O) for the environment. Its low density under normal conditions, the difficulty of storage, and the risk of explosion can summarize the major drawbacks of the use of pure hydrogen as fuel. Also, the other production routes of hydrogen are hydrocarbon reforming and cracking which do not give ultrapure hydrogen and thus, purification needs cost. Moreover, fossil fuels dominate hydrogen production including reforming of natural gas, coal gasification, petroleum coke, or reforming of heavy oil, and is not reliable due to the severe environmental pollution[1].

As mentioned earlier, hydrogen produced by water electrolysis is considered the best method, as it balances between the generation of power source hydrogen fuel from renewable source water and fulfil energy demand for end-use[5] viz. in petroleum refining, ammonia production, metal refining, and electronics fabrication, with an average worldwide consumption of about 40 million tons[6]. Hydrogen provides a sustainable fuel for our future transport requirements/needs and also an approach to the large-scale storage of energy or large-scale production. As per literature, water electrolysis contributes to total hydrogen production of 4 % only worldwide and has been known for around 200 years[7]. However, the water electrolysis produced ultra-pure hydrogen (>99.9%) compared to other methods and thus, the product ultrapure hydrogen is ideal for some high value-added processes such as the manufacture of electronic components[6] and also used as fuel in proton exchange membrane fuel cell (PEMFC). The PEMFC needs ultrapure hydrogen to avoid poisoning of anode Pt electrocatalyst by CO which remains in the hydrogen gas as impurities if the production routes are syngas manufactured from hydrocarbons[8].

Water electrolysis is the process of using electrical energy to split water into hydrogen and oxygen. Usually, water electrolysis unit consists of an anode, a cathode separated by an electrolyte, and an external DC power supply source[4]. Generally, an acidic solution is used as electrolyte in the electrolyzer for water electrolysis. Acidic medium is considered as better electrolyte medium than an alkaline due to high ionic conductivity of an acidic electrolyte and free from carbonate formation as compared to the alkaline medium.

It is seen from the electrolysis reaction (Eq. 1) that anode reaction kinetics plays an important role in hydrogen production at cathode by producing more H^+ ions at anode side which eventually combines at cathode with electron and thereby produces pure hydrogen. Noble metals like platinum (Pt), iridium (Ir), and ruthenium (Ru) are used as anode electrocatalyst which has a strong activity for oxygen evolution reaction but ruthenium (Ru) and iridium (Ir) were passivated at very high potential[9,10]. The best hydrogen evolution reaction electrocatalysts in the order of decreasing catalytic activity are Pt~ Rh >Pd and the order of catalytic activity is Ir ~ Ru >Pd for the oxygen evolution reaction[10]. The bifunctional electrocatalysts can function both for oxygen evolution in electrolysis mode (EL) and oxygen reduction reaction in water fuel cell (FC) mode. The bifunctional oxygen electrocatalyst (BOE) is composed of noble metal oxide such as IrO_2 or Pt-MOx (M = Ru, Ir, Na), bimetallic (Pt-Ir), and trimetallic ($Pt_{4.5}Ru_4Ir_{0.5}$) materials which have been developed as unsupported bifunctional oxygen electrocatalysts[11,12]. The bifunctional oxygen electrode (BOE) and bifunctional hydrogen electrode (BHE) are generally manufactured for the unitized regenerative fuel cell (URFC), so that hydrogen and oxygen could be produced at cathode and anode in the electrolysis mode, whereas in the reverse/FC mode, it could split hydrogen fuel at anode through electrooxidation and combine the H^+ ions, electrons and oxygen at cathode via reduction reaction, thereby producing electricity for the flow of electrons through the outside circuit of the URFC. The simple water electrolyzer splits water molecules at anode to release oxygen, H^+ ions and electrons (Eq. 1) and produce hydrogen at cathode. In a simple electrolyzer, BOE and BHE are not required, as the ultrapure hydrogen gas is only produced in the electrolysis mode. The electrodes are immersed in liquid electrolyte or sandwich of solid membrane electrolyte is made keeping it in between two electrodes and then DC electrical current is passed between two electrode at certain potential. The applied potential must be as low as possible as and little higher than the theoretical open circuit potential (1.23 V). At a set voltage between the electrodes, these electrodes start to produce oxygen gas at anode (Eq. 1) and hydrogen gas at cathode (Eq. 2)[13]. The theoretical decomposition voltage of water 1.23 V is affected by some factors viz temperature, pressure, electrolyte, electrode material, and space between the electrodes[13]. In acid aqueous/liquid electrolyte, water electrolysis occurs at the anode and cathode which are presented by the following equations Eq. 1 and Eq. 2 below[4].

Anode reaction:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \quad \ldots(1)$$

Cathode reaction:

$$2H^+ + 2e^- \rightarrow H_2 \quad \ldots(2)$$

Water electrolysis is the electrochemical reaction in which water is split into oxygen (O_2) and hydrogen (H_2) gas, as in the overall reaction Eq. (3):

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \quad \ldots(3)$$

The basic reaction of Eq. (3) can also be written as[14]:

$$H_2O + \text{Electricity} \rightarrow H_2 + \frac{1}{2} O_2 \quad \ldots(4)$$

According to Grothus conductance or Grothus mechanism, the molar conductance of H^+ and OH^- are much larger than those of other ions. The H^+ and OH^- are highly mobile. The proton can migrate from one water molecule to the next. In the presence of an external electric field, the probability of proton migration in the direction of field increases, and the process will further occur by a chain mechanism, i.e., the movement of a proton from one water molecule to another. With time there is an increase in power consumption, as the applied potential need to be increased at the same current to keep the hydrogen production rate constant and it may be due to the polarization. Moreover, with the progress of the electrolysis process, the pH of the solution increases as the overall reaction results in the loss of H_2O followed by the production of hydrogen and oxygen. In view of this addition of water is also essential for steady production of hydrogen gas. Apart from applied voltage or current in the electrolyzer, the electrocatalyst also play an important role in water electrolysis for better hydrogen production. Generally, iridium (Ir) or its oxides like IrO_2 are recommended as good anode electrocatalysts for splitting of water molecules at low applied DC potential. On the other side platinum (Pt) or Pt based electrocatalyst is used at the cathode side for hydrogen evolution at the cathode side. Using the same electrocatalyst Pt/C at the anode, oxygen evolution reaction takes place at a high voltage which inhibits the use of Pt/C as anode material of the water electrolyzer[17]. Thus, unsupported iridium oxide (IrO_2) is generally used as the alternative to Pt/C[18]. To reduce the loading of iridium oxide, surface area of IrO_2 must be very high. As per literature, iridium oxide (IrO_2) based catalytic layer at anode is significantly stable and shows higher stability in the acidic medium under the oxygen evolution reaction[19,20]. The production of hydrogen gas depends upon the splitting of water molecules at anode as is shown in Eq. 1. It means higher the anode kinetics, higher will be the H^+ ions formation which consequently results in a large amount of hydrogen production at the cathode in presence of Pt/C (Eq. 2). The oxygen evolution reaction (OER) is mainly facilitated by the presence of conductive metal oxides electrocatalysts with IrO_2 and/or RuO_2, are often mixed with inert components to stabilize the structure such as Ta_2O_5, TiO_2, SnO_2, Nb_2O_5, Sb_2O_5, PbO_2, MnO_2[14], or Co_3O_4 [19].

In solid polymer membrane electrolyte electrolysis cells, IrO_2, either pure or mixed with RuO_2[20-26], and IrO_2-Pt[12] composites, have been used for oxygen evolving electrocatalysts, while noble metals like platinum, Pt-CO, Pt-Ni acts as electrocatalysts for the cathode reduction to produce hydrogen gas in acidic solution without reducing to the metals. Apart from this, significant research and intensive efforts have been made for the study on non-noble metals which are mainly alternative to Pt based cathode efficient for hydrogen evolution reaction such as A-Ni-C, Mo_2C/CNTs, Ni_2P/CNTs, Co-doped FeS_2/CNTs, WO_2/C nanowires, and CoFe as well as their alloys/nano-alloys encapsulated in N-doped graphene, etc.[14]. Chakik et al.[13] reported that to produce 6 mL of gas around 2 min 34 s (154 s) using Zn 95% Cr 5% electrode at the applied current of 0.45 A and very high voltage of 5 V using 20 g/lit NaOH alkaline solution as electrolyte. Although, non-noble metals were chosen as electrocatalyst, the applied voltage was very high and thus, it is not economical process. It also implies that the anode electrocatalysts is not efficient in alkaline medium. Lee et al.[15] synthesized IrO_2 as anode in acidic medium of 0.1 M $HClO_4$ and achieved a maximum hydrogen production rate for the applied current 10 mA cm^{-2} at 1.9 V, however the power consumption was too high and efficiency of the electrolytic cell was low. Ma H et al.[16] developed RuO_2 electrocatalyst for acidic medium electrolytic cell for 1 M H_2SO_4 where they were able to get highest hydrogen production at 10 mA cm^{-2} at 1.6 V but the dissolution of Ru metal in electrolyte played a major hindrance in hydrogen production. It is clear from the thorough literature study that the development of an efficient anode for water splitting is the primary need to produce ultrapure hydrogen at a low cost which arises due to low power consumption and at a high rate of hydrogen production. It is also important to determine the optimal concentration of electrolyte where activity of the reaction is maximum with very minimum dissolution of electrocatalyst. It should be noted that the fabrication process along with the anode and cathode electrocatalyst selection are the key aspects of efficient and economical hydrogen production via electrolysis of water. A special emphasis was given to fabricate the electrodes which could improve the electrolysis efficiency and faradic efficiency of the water electrolysis cell.

In this context, in the present study, two-layered composite anode using commercial IrO_2 electrocatalyst, and cathode composites using very low loading of commercial Pt/C electrocatalyst were developed. The electrolyzer performance was investigated using various operating conditions like electrolyte concentration, applied voltage and applied current to determine optimum conditions of the developed electrolyzer at which a higher volume of hydrogen could be produced. The cyclic voltammetry (CV) and electrochemical impedance studies (EIS) of the developed composite anode were performed to check the electrochemical performance in a half cell and also validated the performance in single cell electrolyzer.

Experimental Section

Materials

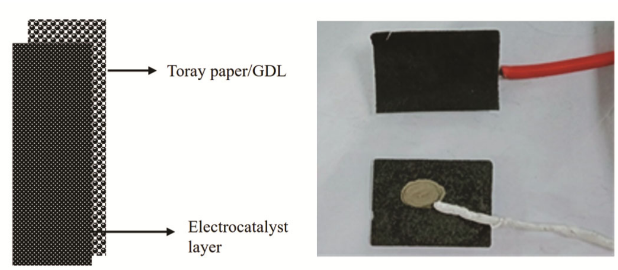
The electrocatalysts used to prepare anode and cathode were IrO_2 (Alfa Aesar, USA) and Pt (40 wt.%)/C_{HSA} (Alfa Aesar, USA), respectively. The Nafion® (5 wt.%) ionomer dispersion (Alfa Aesar, USA) and PTFE (60 wt.%, Sigma Aldrich, Germany) were used as a binder and isopropyl alcohol (Fischer Scientific, India) was used as a solvent to prepare the electrocatalyst ink. The Nafion® ionomer also provides conducting path for the H^+ ions in the electrocatalyst layer. Carbon paper (TGP-H60, Toray, USA) was used as a substrate or gas diffusion layer (GDL) for the painting of electrocatalyst ink to manufacture the electrode to be used in single cell electrolyzer and half cell analysis also. The difference between the electrodes of single cell and half cell was only in size/dimension. Acetylene black (Alfa Aesar, USA) was used for making the electrocatalyst layer conducting for electrons and sulfuric acid (H_2SO_4, 97 wt%, Fisher Scientific, India) dissolved in distilled water was used as an electrolyte.

Electrode fabrication

The anode and cathode electrodes were prepared by painting the electrocatalysts ink on the gas diffusion layer/GDL substrate using a paint brush manually. The electrocatalyst ink for anode was prepared by mixing the required quantity of commercial electrocatalyst IrO_2, Nafion® ionomer, polytetrafluoroethylene (PTFE) dispersion, acetylene black carbon, and isopropanol of required quantity. The mixing of ink composition was done using an ultrasonic bath for 20 min. The prepared anode was dried in a vacuum oven for 1 h at a temperature of 80 °C. The dried anode was further sintered at a temperature of 200 °C for 2 h to get the final form of IrO_2 based composite anode (Fig. 1a). The main purpose of sintering of anode was to make the electrode more porous and active for the splitting the water molecules. The cathode electrocatalyst ink was prepared similarly to that of an anode and painted on GDL to get the cathode. The electrode manufacturing and sintering of cathode was also done in a similar way as that of anode. The electrocatalyst loading of both electrodes was 1 mg/cm^2. The electrocatalyst and acetylene black carbons were taken of 1:1 ratio. The surface area of the active electrodes, i.e., anode and cathode, was 5 cm × 1 cm. Images of the anode and cathode are shown in Fig. 1b.

Experimental setup and method for single-cell electrolyzer

The experimental setup of electrolyzer approximate volume of 5 L was fabricated using a perspex sheet in which two wires were used for both the electrodes to connect it with a direct current (DC) electric/power source (Fig. 2a). The electrodes were then attached to the wires using conducting material i.e., silver paste (Fig. 1b). The electrolyzer unit made of perspex sheet was half-filled with different concentrations of electrolyte/H_2SO_4. The electrodes were covered with plastic gas storage to store product gases i.e., hydrogen from cathode and oxygen from anode. As the product gas pressure affects the electrochemical reactions as per the Nernst equation, the cathode pressure was maintained similar to anode. The gas storage was open at the bottom and sealed at the top to store gas. Both storages were placed upside down



(a) (b)

Fig. 1 — (a) Schematic of two layered composite anode and (b) photographic view of both electrodes connected with wire using silver paste

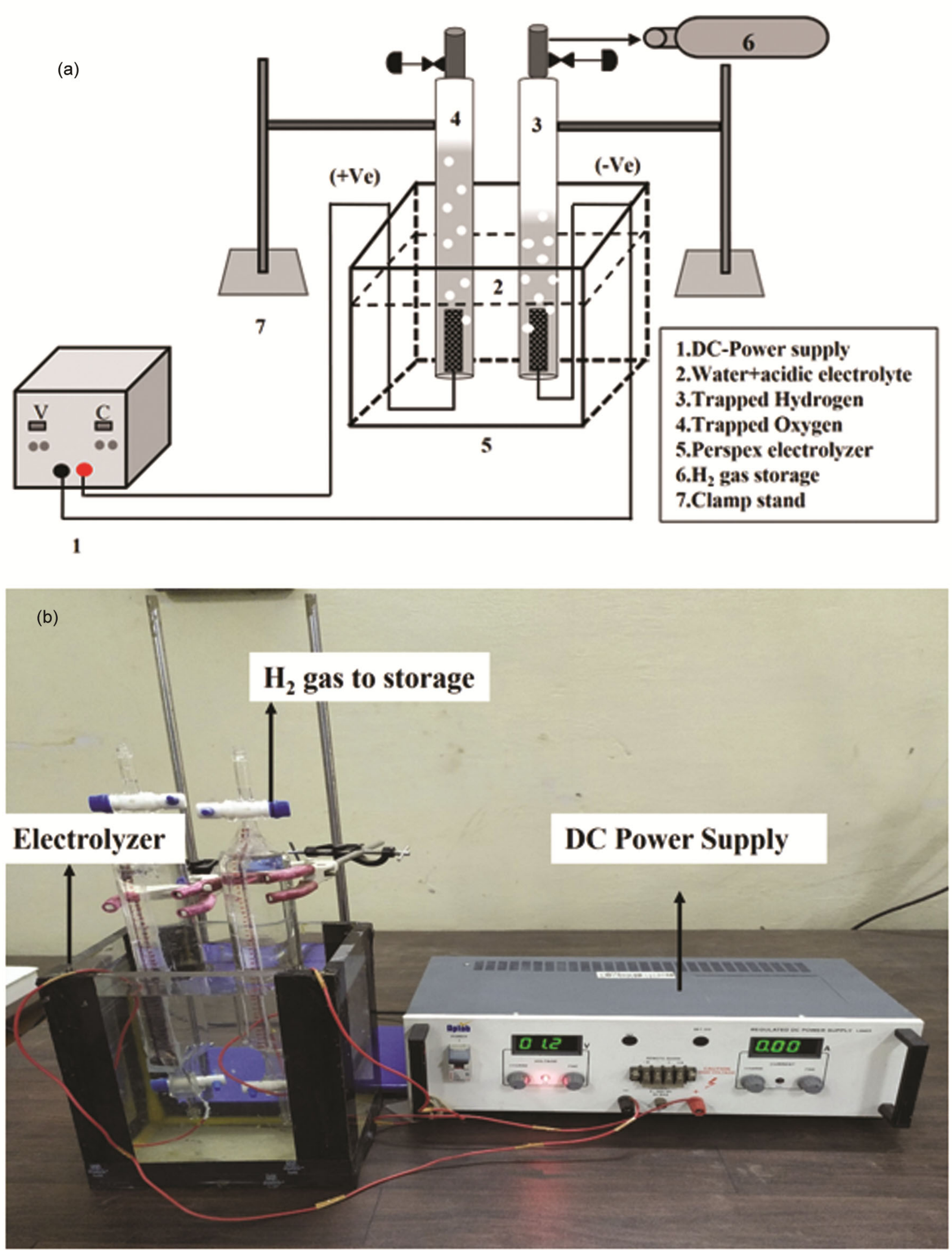


Fig. 2 — (a) Schematic of experimental setup of electrolyzer for hydrogen production and (b) photographic view of experimental setup of electrolyzer with DC power supply

so that it can be used as a cover for electrodes and could have been filled with water more than 30%.

The electric supply in the range of 1.6 V to 2.3 V was used so that electrolysis of water takes place with the formation of hydrogen and oxygen gas at a very low DC power supply. The product hydrogen gas was then collected by downward displacement of water method at the cathodic storage. In case of collection for further use, a pipe could be connected from the storage and adsorbed in a metal hydride tank.

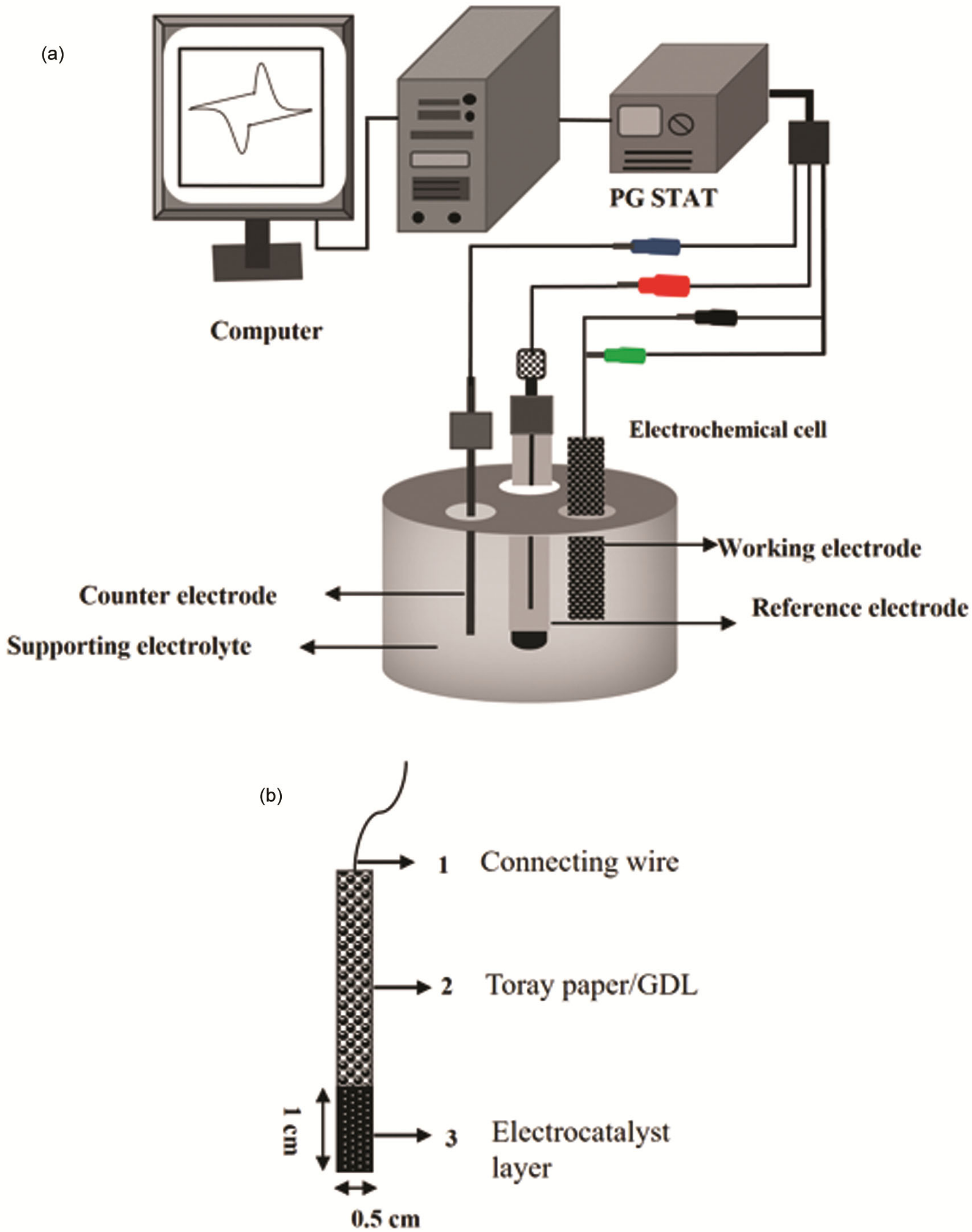


Fig. 3 —Schematic of (a) cyclic voltammetry and (b) working electrode for electrochemical investigation

Electrochemical analysis of composite anode

The electrochemical experiments were carried out at ambient temperature of 20 °C in a typical half-cell consisting of three-electrode system (Fig. 3a) viz reference electrode (Ag/AgCl), working electrode/IrO_2 composite electrode and platinum counter electrode. The working electrode was made of GDL/carbon paper (TGP-H-60, Toray) coated with IrO_2 (Fig. 3b). The loading of electrocatalysts at working electrode was maintained 1 mg/cm^2 of IrO_2. The electrode was prepared using electrocatalyst ink made of 0.5 mg of electrocatalyst in 5 wt % Nafion® solution (5 µL) and one drop of PTFE solution with the help of a syringe. The nitrogen gas from cylinder was purged to the aqueous H_2SO_4 solution of various concentrations viz 0.25 M, 0.50 M, and 0.75 M purged for 30 min before each experiment to remove dissolved oxygen from the electrolyte solution. The potentiostatgalvanostat/PGSTAT system (PGSTAT 204, Autolab, Netherland) equipped with FRA potentiostat module and controlled via NOVA 1.10 software was used to perform electrochemical measurements of the developed anode[35]. The CV measurements were performed in the voltage range from -0.5 V to 1.5 V at a scan rate of 50 mV s^{-1}. The EIS was perform by working electrode at a constant of -0.05 V vs RHE with the frequency ranging from 100 kHz to 0.1 Hz with a 10 mV amplitude of AC signal[25].

Results and Discussion

Half cell analysis

Effect of electrolyte concentration

Fig. 4a shows the electrochemical behaviour of the fabricated composite anode electrode for the CV studies in the voltage range from -0.5 V to 1.5 V using varying electrolyte concentration ranging from 0.25 M to 0.75 M of H_2SO_4 solution with a fixed scan

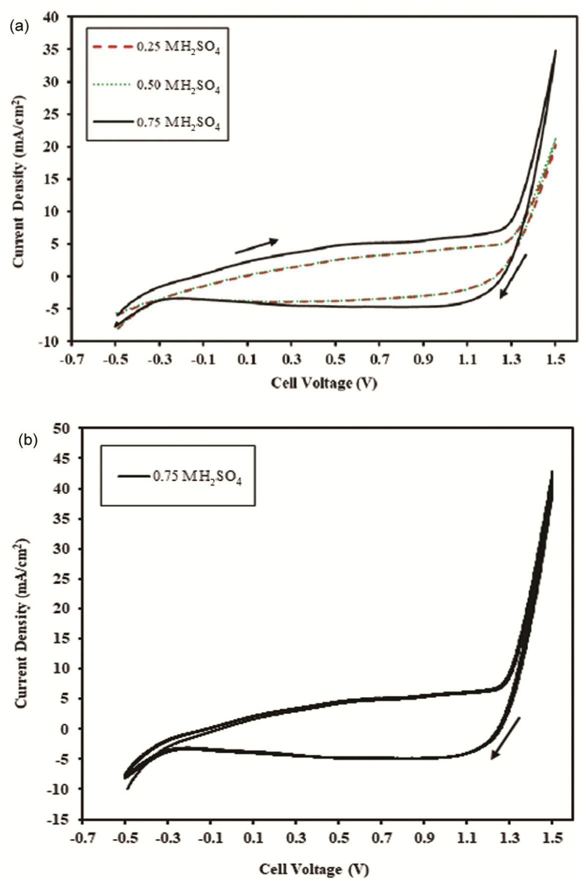


Fig. 4 — Cyclic voltammograms of IrO_2 composite anode for (a) (1 cycle) using different concentration of H_2SO_4 electrolyte and (b) (by 20 cycle) using 0.75 M H_2SO_4 at a potential scan rate of 50 mV s^{-1} with electrocatalyst loading 1 mg/cm^2 IrO_2 and temperature : 20 °C

rate of 50 mV s^{-1}. The cyclic voltammograms of IrO_2 shows much higher peak current density at 0.75 M H_2SO_4, while the lower electrolyte concentration of 0.25 M H_2SO_4 shows a lower peak current density. This may be due to the increased reaction kinetics at acidic medium with relatively higher concentration of H_2SO_4. Moreover, availability of ions increases with the increase in electrolyte concentration which results in lower charge transfer resistance at the electrode electrolyte interface and there by enhanced reaction kinetics[28]. It is seen from the Fig. 4a that the same current density of approximately 20 mA /cm^2 for 0.25 M and 0.50 M electrolyte and about 35 mA /cm^2 for 0.75 M H_2SO_4 electrolyte were obtained at the voltage 1.5 V. The decrease in the current density for both 0.25 M and 0.50 M electrolytes could be due to a low concentration of the H_2SO_4 electrolyte on the electrode surface and low ionic mobility in the electrolyte solution. The high current density (35 mA /cm^2) for higher concentration of electrolyte (0.75 M) indicates better performance of the electrode at this concentration in electrolyzer.

It is important to understand the reaction kinetics at anode as it is the most sluggish process of the electrolytic cell. The CV curve obtained in the present study closely matches with the CV reported by Pfeifer et al. (2017)[28]. They worked on finding the oxygen evolution reaction (OER) mechanism on IrO_x surface at anode (Eq. 5- Eq. 7). The CV of a IrO_x electrode displays the characteristic oxidation waves at 1 V vs. SHE (standard hydrogen electrode) commonly attributed to an oxidation of Ir^{III} to Ir^{IV} [29] and around 1.3 V vs. SHE where it presents the oxidation of oxygen i.e., O^{II-} contained in the IrO_x matrix in the form of adsorbed OH groups, to O^{I-} and the OER onset at 1.5 V vs. SHE[31]. The electrooxidation of water at anode proceeds through several steps as presented below.

Water adsorption (where Ir^{III} to Ir^{IV} transition occurs):

Water molecule (H_2O) adsorbs onto the catalyst surface or adsorbent site (S) and loses a proton (H^+) and electron, forming a hydroxyl radical (OH) attached to the surface.

$$Ir^{III}O_x + H_2O \rightarrow Ir^{IV}O_x\text{ -}O^{II-}H + H^+ + e^- \qquad \ldots(5)$$

Oxidation of O^{II-} to O^{I-} :

The oxidation of O^{II-} present in the IrO_x matrix as adsorbed OH group undergoes oxidation to form O^{I-} which is highly reactive and prone to nucleophilic attack

$IrO_x\text{-}O^{II\text{-}}H \rightleftharpoons IrO_x\text{-}O^{I\text{-}} + H^+ + e^-$ …(6)

Oxygen evolution reaction:

The electrophilic nature of the O^{I-} makes this nucleophilic attack of water possible.

$IrO_x\text{-}O^{I\text{-}} + H_2O \rightarrow IrO_x\ O^{I\text{-}}\text{-}O^{I}H + H^+ + e^- \rightarrow IrO_x + O_2 + 2H^+ + 2e^-$ …(7)

The H^+ ions travel through the electrolyte of 0.75 M H_2SO_4 which leads to hydrogen evolution reaction occurring at cathode (Eq. 8- Eq.10). While HER is a fast reaction and has low activation overpotential in acidic environments where it follows Volmer-Heyrovsky-Tafel mechanism[32], involving three principal steps:

Volmer step: Here incoming H^+ adsorbs onto the catalyst surface (S) and accepts an electron, becoming an adsorbed hydrogen atom.

(S-H): $S + H^+ + e^- \rightarrow S\text{-}H$ …(8)

Heyrovsky step: In this step, another H^+ donates a proton to an already adsorbed hydrogen atom on the surface, forming hydrogen gas (H_2).

$S\text{-}H + H^+ + e^- \rightarrow H_2 + S$ …(9)

(or)

Tafel step: Where two adsorbed hydrogen atoms directly combine to form hydrogen gas and desorb from the surface:

$2\ S\text{-}H \rightarrow H_2 + 2\ S$ …(10)

Fig. 4b shows the CV for 20 cycles in continuous scan at the suitable electrolyte concentration of 0.75 M and scan rate of 50 mV s^{-1}. It is seen from the Fig. 4b that the broad shoulder region from -0.3V to 0.9V shifted slightly upward in the forward scan and shifted slightly in the downward direction with progress of number of cycles indicating stable IrO_2 anode composite with little more active electrode surface for longer duration of electrolysis operation. Such pattern of CV of the IrO_2 electrode accurately exhibits pseudocapacitive behaviours. The CV capacitance contains contributions from double-layer capacitance and pseudocapacitance, which depend on surface area of the electrode[27]. The IrO_2 composite electrode in the voltage region of -0.3 V, showed the increased redox current of 1.806 mA/cm^2 for the CV of 20 cycles. The enhancement of the peak current density at higher cycle is due to the electrocatalyst activation. The anode displayed stability and was highly active under acidic conditions without undergoing corrosion or leaching as shown by Fig. 4b for OER reactions even after 20 cycles which is extremely challenging in acidic conditions. The potential regions for OER also do not shift from the initial position due to good stability of the developed electrode.

Stability test and EIS analysis of composite electrode

The EIS is a powerful tool for exploring the surface properties and electrochemical interfacial behaviour of electrolyte-electrode interface. Fig. 5a shows the Nyquist diagrams obtained through EIS for the IrO_2 anode composite in varying electrolyte concentrations in a single cycle. It is seen from the Fig. 5a that the arc radius of higher concentration (0.75M) of H_2SO_4 electrolyte is lower than arc radius obtained for the 0.25 M and 0.5 M of H_2SO_4. The semicircle with small radius of the EIS characteristic are indicating low charge transfer resistance, whereas, the semicircle with large radius are showing high charge-transfer

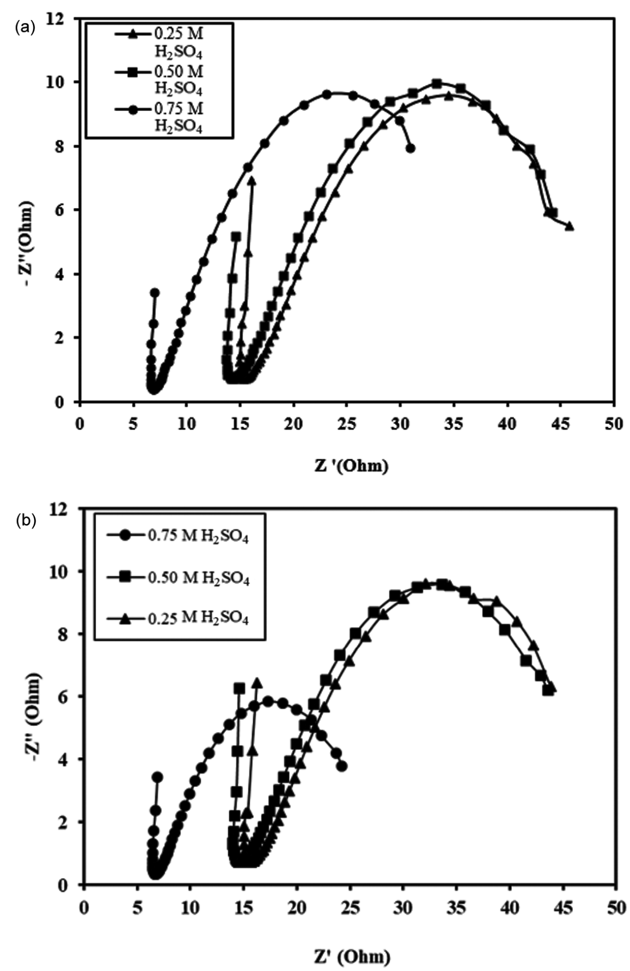


Fig. 5 — Nyquist plots of (a) Fresh, (b) 20 Cycle IrO_2 composite anode electrode at potential rates 1.28V in different concentration of electrolyzer 0.25 M H_2SO_4 , 0.50 M H_2SO_4 and 0.75M H_2SO_4 with electrocatalyst loading 1 mg/cm^2 ; Temperature : 20 °C

resistance at the electrode-electrolyte interface[34]. The charge transfer resistance is always low for the high concentration of electrolyte of 0.75 M, irrespective of number of cycle use[35]. It may be due to higher mobility of ions at this concentration.

The EIS of fresh electrode and after 20 cycles of CV were compared keeping the electrolyte concentration fixed at suitable value of 0.75 M (Fig. 6). It is seen that the charge transfer resistance becomes low with the increase in number of CV cycles. The reason for lower charge transfer resistance with the increasing CV cycles may be due to increased activity of the electrode and lesser deposition of intermediate species on the electrode surface and thereby giving lower charge transfer resistance.

All the Nyquist plots of IrO_2 at 1.28 V (vs. RHE) for varying electrolyte concentration were recorded in the frequency range from 0.1 Hz to 100 kHz, and the impedance data obtained were fitted using the equivalent electrical circuit model . Fig. 7 shows the sample EIS characteristic for 20 cycle with 0.75 M electrolyte concentration and equivalent circuit obtained through Z-view software to find out Solution resistance Rs, Charge transfer resistance between electrode and electrolyte interface Rct and the constant-phase element i.e., double-layer capacitance at the interface of electrolyte and electrocatalyst represented by CPE, and CPE–T is a pseudocapacitance or CPE-P is related to the semicircle in Nyquist plot. The Rct is the measurement of the semicircle arc diameter which is associated with the obstruction of passing of electrons at the interface of the electrode and electrolyte interface. The measured data obtained from the equivalent circuit are presented ion Table 1 is fairly consistent with the trend of EIS plot which are already discussed in Fig. 5.

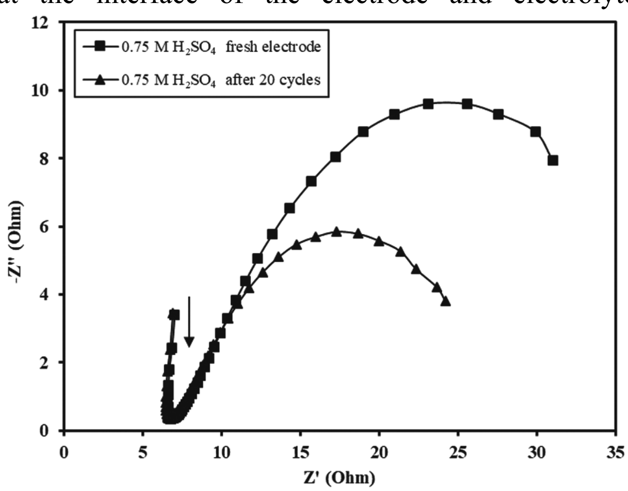


Fig. 6 — Nyquist plots of IrO_2 composite anode electrode at potential rates 1.28 V fresh and after 20 cycles in a concentration of electrolyte 0.75 M H_2SO_4 with electrocatalyst loading of 1 mg/cm^2; Temperature : 20 °C

It is seen from the Table 1 that the lowest charge transfer resistance (Rct) of 61.6 Ω was found for the relatively higher concentration of electrolyte of 0.75 M. The solution resistance (Rs) was also found lowest (6.539 Ω) for the same electrolyte concentration of 0.75 M.

The Nyquist plots were analyzed in a depressed shape with semicircles. It is seen from Fig. 6 that the electrolyte H_2SO_4 concentration of 0.75 M exhibit the lower charge transfer resistance of electrodes after 20 cycles of cyclic voltammogram, while the fresh electrode of 0.75 M electrolyte concentration exhibit the higher charge transfer resistance. However, the arc diameter of the Nyquist plots increases dramatically when the impedance spectra of the electrode are performed after 20 cycles of continuous CV tests. The diameter of the semicircles obtained during the experiments indicates the charge transfer resistance of the composite electrode under the study[35]. It shows that the charge transfer resistance after 20 cycles of a composite electrode is higher than the fresh electrode irrespective of the concentrations of H_2SO_4 electrolyte. The total resistance of the electrode is affected by the electrode spacing, electrolyte concentration, and electrical conductivity. The value of CPE /double-layer capacitance (dl) is 0.49 mF and 0.0355 mF for CPE –P and CPE- T respectively. The value of Rct is 61.6 Ω. Thus, the overall ohmic resistance of the electrode was measured at the high-frequency real axis intercepts of the Nyquist plot (Fig. 7) and it was in the range of 6.539 Ω.

Single-cell electrolyzer study

Effect of current on hydrogen production

The hydrogen gas produced at the cathode was clearly seen to liberate from the surface of the electrode and after coalescence of the product, bubbles floated at the surface followed by storage at the cathode. The hydrogen gas bubbling was seen to

Table 1 — Electrochemical impedance properties R_s, R_{ct} and C_{PE} of IrO_2 composite electrode obtained by fitting the experimental value to equivalent circuit after 20 cycles of CV

H_2SO_4 electrolyte concentration (M)	R_s (Ω)	C_{PE-T} (m F)	C_{PE-P} (m F)	R_{ct} (Ω)
0.75	6.539	0.0356	0.4919	61.6
0.50	14.2	0.0208	0.4618	101.6
0.25	15.25	0.0207	0.4654	86.37

be at a high rate when there was an increase in the current supply or voltage across the electrolyzer. An increase in the bubbling of gas was also seen when the electrolyte concentration was increased.

Fig. 8a shows the volume of hydrogen production with time for different currents applied across the electrodes. The electrolyte concentration was 0.25 M H_2SO_4. It is seen from Fig. 8a that hydrogen production increases with the increase in time irrespective of the applied current. However, the highest amount of hydrogen (10 mL) was produced in a very short time of 882 s (14 min 42 s) when the highest amount of current i.e., 0.1 A (2.3 V) was applied. For the same amount of hydrogen gas (10 mL) production, the required time was very high 2305 sec (38 min 25 s) when an applied current was low i.e., 0.04 A (1.9 V) only (Table 2). It should also be noted that at the theoretical amount of applied voltage of 1.23 V, there was no formation of bubbles at the surface of electrode. The bubbling was seen to start at 1.5 V irrespective of the concentration of electrolyte due to high overpotential and large ohmic voltage drop[36]. While the electrolysis of water is thermodynamically feasible at 1.48 V, in reality, the reaction occurs prohibitively slowly and further potential must be applied to accelerate the reaction to a practical rate.

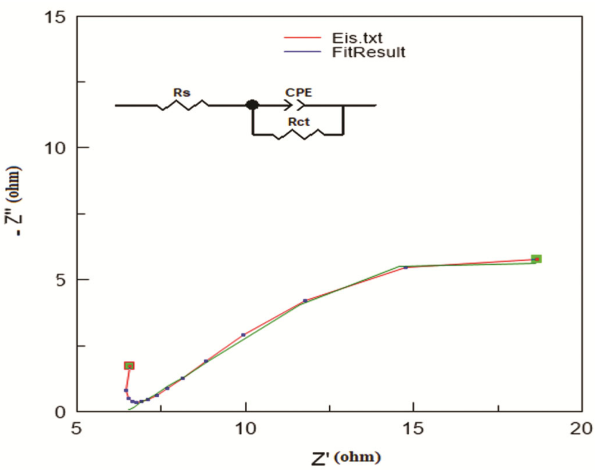


Fig. 7 — Equivalent circuit to measured spectra using Z-View 4 data software and value of R_{ct} used to fit the EIS data; 0.75 M H_2SO_4 electrolyte; 20 cycles of CV

Fig. 8b and Fig. 8c show the hydrogen production with time for varying applied current across electrodes at higher concentration of electrolyte i.e., 0.50 M H_2SO_4 (Fig. 8b) and 0.75 M H_2SO_4 (Fig. 8c), respectively. It is seen from the Fig. 8b and Fig. 8c that the hydrogen volume of 10 mL were obtained in 720 sec (12 min) (Table 3) and 675 sec (11 min 15 s)

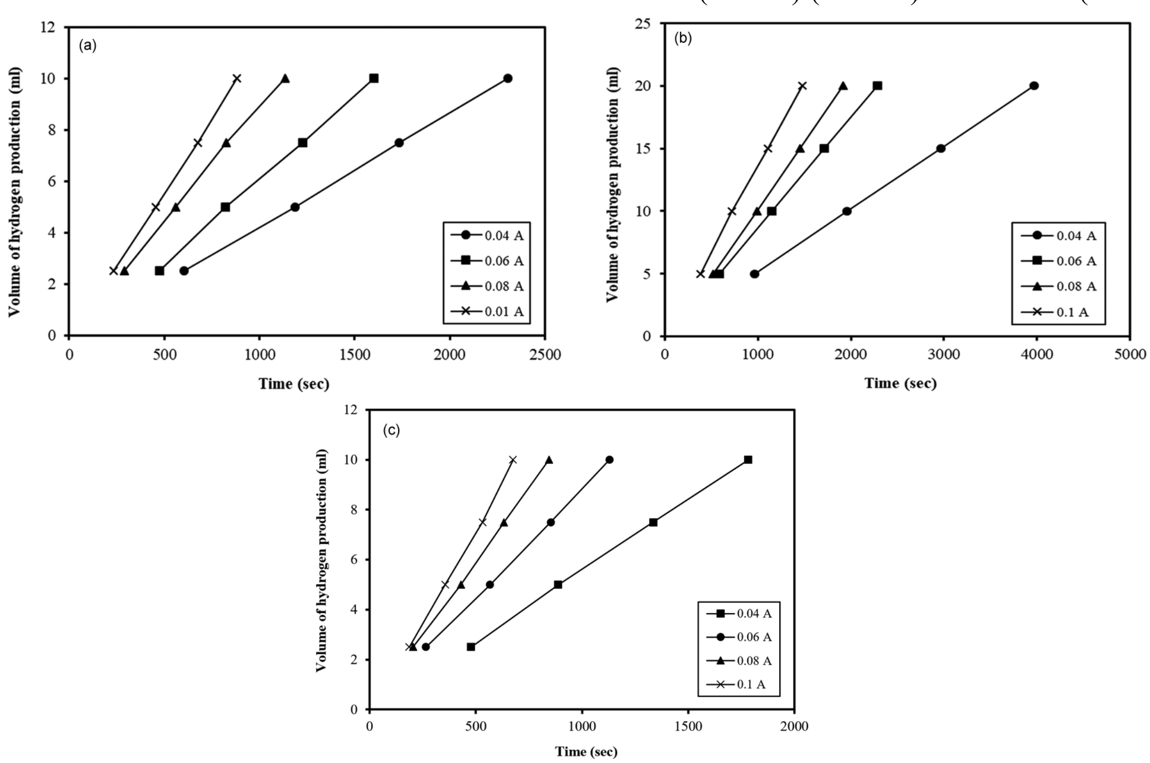


Fig. 8 — Volume of hydrogen production in (a) 0.25 M, (b) 0.50 M and (c) 0.75 M H_2SO_4 electrolyte for varying applied current and corresponding voltage

(Table 4) for the applied current of 0.1 A (2.2 V) and 0.1 A (1.9 V) using electrolyte concentration of 0.50 M and 0.75 M H_2SO_4, respectively. The increase in electrolyte concentration decreased the production time of hydrogen due to increase in electrolyte concentration from 0.25 M to 0.75 M H_2SO_4.

Moreover, the production of hydrogen was found to be a linear function of time with very little deviation from linearity. Thus, the rate of production of hydrogen was approximately constant for a given concentration of electrolyte at a constant current supply. This trend is seen in all characteristics (Fig. 8a to Fig. 8c). It should also be noted that product of applied current and corresponding voltage in the electrolyser gives applied external power which is decreasing consistently with the increase in the electrolyte concentration from 0.25 M to 0.75 M. Thus, it is seen from Table 2 to Table 4 that the applied power decreases from 0.23 watt to 0.19 watt with decreasing time requirement from 882 s to 675 s for the same amount (10 mL) of hydrogen production.

Table 2 — Time required for hydrogen production at different applied current and corresponding voltage using IrO_2 anode and cathode Pt/C in 0.25 M H_2SO_4 solution

Volume of hydrogen production (mL)	Applied current and voltage			
	0.04 A/ 1.9 V	0.06 A/ 2.1 V	0.08 A / 2.2 V	0.1 A/ 2.3 V
	Time (s)	Time (s)	Time (s)	Time (s)
2.5	603	475	292	235
5	1188	822	558	464
7.5	1735	1225	826	678
10	2305	1600	1135	882

Table 3 — Time required for hydrogen production at different applied current and corresponding voltage using IrO_2 anode and cathode Pt/C in 0.50 M H_2SO_4 solution

Volume of hydrogen production (mL)	Applied current and voltage			
	0.04 A & 1.8 V	0.06 A & 2 V	0.08 A & 2.1 V	0.1 A & 2.2 V
	Time (s)	Time (s)	Time (s)	Time (s)
5	964	585	517	385
10	1960	1150	993	720
15	2965	1714	1450	1105
20	3970	2284	1912	1480

Table 4 — Time required for hydrogen production at different applied current and corresponding voltage using IrO_2 anode and cathode Pt/C in 0.75 M H_2SO_4 solution

Volume of hydrogen production (mL)	Applied current and voltage			
	0.04 A/ 1.6 V	0.06 A/ 1.7 V	0.08 A/ 1.8 V	0.1 A/ 1.9 V
	Time (sec)	Time (sec)	Time (sec)	Time (sec)
2.5	478	265	205	187
5	888	567	430	355
7.5	1335	853	633	532
10	1783	1129	844	675

Voltage-current trends at various electrolyte concentrations

The voltages versus current characteristics were also studied for different concentrations of the electrolyte varying from 0.25 M to 0.75 M. It is seen from Fig. 9 that the voltage versus current plot shifted downward with the increase the in electrolyte concentration. This study (Table 5) shows that the 0.75 M H_2SO_4 is more preferable condition of the electrolyzer as required voltage is low at very high applied current (Table 5), whereas, lower concentration of electrolyte i.e., 0.25 M and 0.50 M H_2SO_4 need progressively higher voltage at the same applied current. It indicates that more power will be required for the lower concentration of electrolyte to produce the same amount of hydrogen keeping other parameters constant. The decrease in voltage with an increase in concentration of electrolyte at constant current

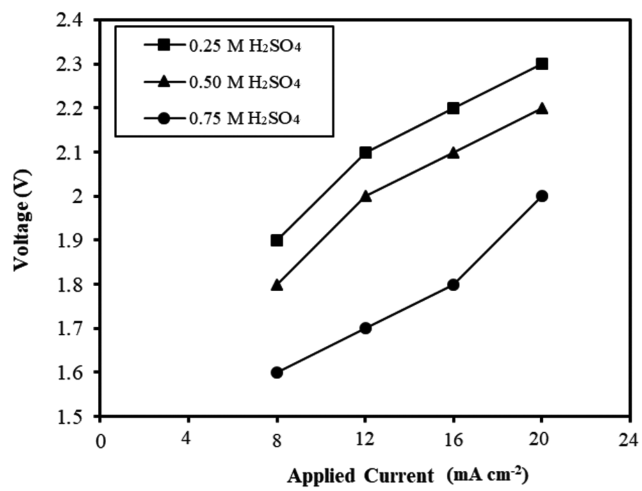


Fig. 9 — Trend of applied current vs voltage with varying electrolyte concentration for IrO_2 anode and Pt/C cathode at the electrolysis temperature of 20 °C

Table 5 — Applied current vs voltage data with varying electrolyte concentration for IrO_2 anode and Pt/C cathode

Applied current A or (mA cm^{-2})	Concentration of H_2SO_4 electrolyte and voltage		
	0.25 M	0.5 M	0.75 M
	Voltage (V)	Voltage (V)	Voltage (V)
0.04/ (8)	1.9	1.8	1.6
0.06 / (12)	2.1	2	1.7
0.08/ (16)	2.2	2.1	1.8
0.1/ (20)	2.3	2.2	1.9

is mainly due to the increase in mobility of ions hence, resulting in a decreased resistance of the electrolyte.

Effect of electrolyte concentration on hydrogen production

Fig. 10 shows the effect of electrolyte concentration on hydrogen production. It is clearly seen from Fig. 10 that the rate of hydrogen production was highest (0.9 mL/min) for the electrolyte concentration of 0.75 M H_2SO_4 and applied current of 0.1 A. For the same concentration of 0.75 M H_2SO_4, the production rate of hydrogen decreased to 0.33 mL/min when the applied current was low (0.04 A) (Table 4). The lowest hydrogen production rate of 0.68 mL/min was recorded for the electrolyte concentration of 0.25 M H_2SO_4 at an applied current of 0.1 A (Table 6). At the same concentration of 0.25 M H_2SO_4, the production rate of hydrogen decreased to 0.26 mL/min when an applied current was maintained at 0.04 A (Table 2). A similar effect on hydrogen production was also noticed for the electrolyte concentration of 0.50 M H_2SO_4. Although the high concentration of electrolyte gives a higher production rate of hydrogen for any applied current, the concentration of electrolyte should not be increased to high. It can lead to corrosion problems of the various cell components which will result in the low life of the electrolyzer. Thus, a balance is required between all parameters for getting hydrogen for a longer period without any degradation of the electrolyzer.

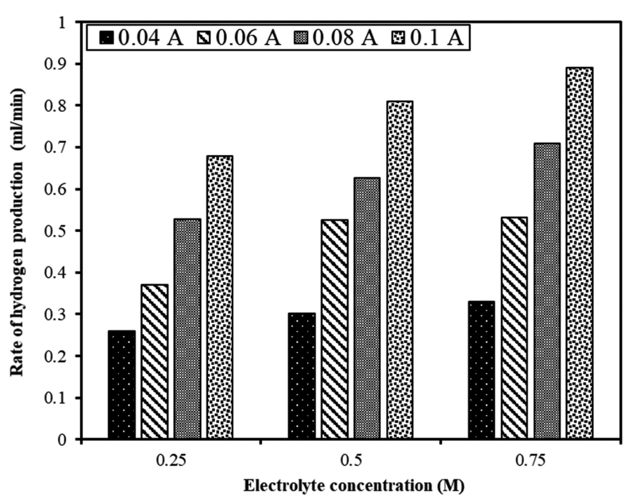


Fig. 10 — Hydrogen production rate with varying concentration of H_2SO_4 electrolyte at different current supply

Table 6 — Time required for 10 mL of hydrogen production for varying electrolyte concentration and highest applied current of 0.1 A in the electrolyzer using IrO_2 anode and Pt/C cathode

Volume of H_2SO_4 electrolyte (M)	Voltage at highest applied current (V)	Time (s)
0.25	2.3	882
0.50	2.2	720
0.75	1.9	675

It is clearly seen from the Table 6 that the required time to produce hydrogen of 10 mL for composite IrO_2 anode decreases with the increased electrolyte concentration and also the required voltage is decreasing consistently for the applied current 0.1 A. It may be due to the increasing electrolyte concentration leads to an increase in the electrical conductivity of the electrolyte solution and consequently enhances electrochemical reaction kinetics at the electrodes for hydrogen production[37, 38].

In the present work, the water electrolyzer was successfully developed for the production of ultrapure hydrogen at high faradic efficiency[39] and electrolytic efficiency[40]. The Faradic efficiency for developed setup was around 88 % and electrolytic efficiency was around 75 %, which shows excellent performance of the fabricated electrodes by painting the electrocatalyst ink on gas diffusion layer by paint brush method in the present study. The concentration of electrolyte played a key role in controlling the performance of our water electrolysis cell as it shown by the high electrolytic and faradic efficiency. When the concentration of H_2SO_4 was 0.25 M and 0.5 M the rate of OER was low and it has also been mentioned in literature when the electrolyte concentration is high there is significant degradation or dissolution of anode catalyst[41]. Pauporté et al.[42] showed that when H_2SO_4 of 1M was used as electrolyte there was significant dissolution of IrO_2 which affected its activity. However, in the present work, the rate of OER was maximum when the concentration of electrolyte of 0.75 M was used without IrO_2 undergoing any significant degradation which led to finding the optimum concentration of electrolyte where both high activity and stability was observed.

Conclusion

It is seen from the present study that the IrO_2 composite anode is electrochemically very active to split the water molecules at very low current and voltage. Thus, the power consumption is very low. The cathode electrode is equally good as that of the anode. The highest hydrogen production rate of 0.9 mL/min was obtained at a voltage of 1.9 V and a current of 0.1 A using the electrolyte concentration of 0.75 M H_2SO_4. However, the hydrogen production rate was very low (0.33 mL/min) when a low voltage of 1.6 V and current of 0.04 A was applied at the same concentration of electrolyte (0.75 M) H_2SO_4. The rate of production of hydrogen increases with an increase in the current applied due to an increase in the formation of hydrogen ions. It was the preliminary study using the developed composite anode which could be used after replacement of liquid acid-based electrolyte with the solid proton exchange membrane (PEM) electrolyte in the electrolyzer to produce a high rate of hydrogen without any corrosion problem, as PEM is solid and has very high ionic conductivity.

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