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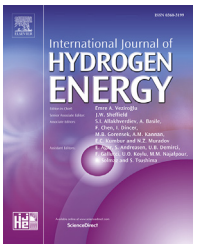

Enhanced hydrogen generation by water electrolysis employing carbon nano-structure composites

C.R.P. Patel, Prashant Tripathi, Alok.K. Vishwakarma, M. Talat, Pawan K. Soni, T.P. Yadav, O.N. Srivastava [*]

Hydrogen Energy Centre, Physics Department, Banaras Hindu University, Varanasi, 221005, India

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ABSTRACT

The present study describes the hydrogen generation through electrolysis by using graphene-carbon nanotube (GC) nano-composite electrode. Synthesis of GC nano-composites of various compositions utilizing solution admixing approach has been done. Structural, morphological, microstructural and analysis of quality of various carbon nano-composites have been investigated by using XRD, SEM, TEM, Raman and FTIR techniques. To determine the electrochemical catalytic performance of GC composites, these have been used as working electrode (anode) for electrolysis of water in an alkaline medium (1 M NaOH). The results reveal that the GC73 (70 wt% graphene and 30 wt% CNT) nano-composite is an optimum anode material for hydrogen production. The highest hydrogen production rate of 487 l/h-m^2 has been observed for the composite GC 73. Based on Tafel plot and FTIR characterizations, a feasible mechanism for this high hydrogen yield has been put forward.

Introduction

Hydrogen in sharp contrast to fossil fuels is renewable, clean, climate friendly and inexhaustible fuel produced from water by a variety of input energies. Hydrogen burns back to water after use in IC engine or fuel cell [1–3]. Decentralized electrolysis of water is thought to be one of the best options for use of hydrogen in localized small utilities like two wheelers and home cookers. Water electrolysis is one of the optimum modes of hydrogen production through dissociation of water (H_2O) into H_2 and O_2 on cathode and anode, respectively. This method has the advantage of producing extremely pure hydrogen. However, water electrolysis methods contribute only 4% of total hydrogen production [4]. A major limitation of water electrolysis for hydrogen production is the poor reaction kinetics of oxidation of hydroxyl ions (OH) into oxygen at the electrode (anode). Rather high over-potential is required for the reaction to take place at a reasonable rate. Because of the over-potential and ohmic losses, actual potential required exceeds the standard potential of 1.23 V for water electrolysis [5–9]. The potential required is generally ~1.8 V–~2.0 V. One of the efforts in the direction of lowering over-potential and hence improving the hydrogen production rate is to select suitable electrode materials, which may lead to lower activation energies for the reaction to take place. Among various

* *Corresponding author.*
E-mail address: heponsphy@gmail.com (O.N. Srivastava).

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feasible materials used for electrodes, carbon nanostructures seem to be the material of choice [10–16] because of its low cost, better electrical and thermal conductivity, stability in alkaline electrolyte as compared to metals and also for its large effective surface area [17,18]. Recently, there have been several studies on the use of carbon nano-structure electrodes as catalysis of various electrochemical reactions [18–27]. Carbon nanotubes and graphene, because of their unique electronic properties, have attracted attention for their application as efficient electro-catalyst. Kostov et al. [26] have studied thermal dissociation of water and based on theoretical considerations, they have shown that the water dissociation temperature gets lowered to about 1000 K in the presence of CNTs, whereas the temperature required is ~2000 K when graphite is used as catalyst. Guo et al. [27] studied water dissociation on charged defective single walled carbon nanotubes and found that charged carbon nanotubes had activation barrier of ~0.167 eV between the transition state and the reactant. Guo et al. attributed decrease of the activation barrier due to interaction of π-electron of CNTs and water molecules.

In an earlier work, we reported hydrogen production through electrolysis using CNTs as electrode in a conventional alkaline water electrolysis cell at anodic voltages as low as ~1 V (vs. SCE) [28]. The hydrogen production rate with the CNTs was found to be nearly double of that obtained from traditional graphitic carbon anodes under identical conditions. The high hydrogen production rate was shown to be caused by defects on the nanotubes which results in the reduction of the energy barrier for the dissociation of OH into oxygen at the anode [28]. It should be pointed out that enhancing the efficiency of electrolysis will increase efficiency of hydrogen production. For decentralized hydrogen production through conventional grid electricity (preferably for off-peak electricity) where hydrogen is the product produced (at cathode) together with oxygen (at anode) increasing efficiency of electrolysis will increase cost effectiveness of hydrogen. For hydrogen production via electricity coming from renewable sources e.g. wind electricity or photovoltaic electricity, enhancing efficiency of electrolysis will again produce cost competitive hydrogen. As for example, efficiency of commercial PV electricity production is ~15%, if for electrolysis conventional electrolyzer with efficiency of about 50% the efficiency of hydrogen production will be ~7.5%. However, if the efficiency of electrolysis is increased to 70%, the efficiency of hydrogen production will shoot up to 10.5% as outlined in the following:

$$\eta_{h.p.} = \eta_{pv} \text{ x } \eta_{electrolysis}$$

$$= 15\ \% \times 50\ \% = 7.5\%$$

$$\eta_{h.p.} = \eta_{pv} \text{ x } \eta_{electrolysis} \uparrow 50 \text{ to } 70$$

$$= 15\ \% \times 70\ \% = 10.5\%$$

Encouraged by the work on hydrogen production by using of CNTs as anode material, we proceeded to use the well-known carbon nanostructure, the graphene as an electrode (anode). The choice of graphene was made keeping in view the fact that the surface area of graphene is higher than that of CNTs [29,30]. Anode made of graphene pellet having similar geometry as the CNT anodes were employed. However, for graphene anode under anodic voltage of ~1 V, surprisingly the hydrogen production rate was found to be lower. Careful microstructural studies of graphene anodes revealed that the low hydrogen production rate was due to agglomeration of graphene flakes. We have tried to avoid this agglomeration by making composites of graphene and CNTs where CNTs work as thread like separating graphene sheets. This avoids agglomeration of graphene sheets. It has been observed that with the GC composite material used as anode, where graphene flakes do not agglomerate, the rate of hydrogen production has been found to be ~30% higher than that with CNT anode.

Experimental method

Synthesis of graphene

Graphene was synthesized by modified Staudenmaier's method using reacting graphite powder with a mixture of conc. sulphuric and nitric acids in 2:1 ratio with potassium chlorate at room temperature. Further washing (with 5% HCl) and filtration is done which is followed by vacuum drying. Graphite oxide powder so obtained is subjected to thermal exfoliation at 1050 °C under Ar atmosphere. This leads to the promotion of graphene (which is also known as graphene oxide). Details are given elsewhere [31,32].

Synthesis of carbon nanotubes

CNTs have been synthesized using spray pyrolysis chemical vapor deposition (CVD) method described by us earlier [32–34]. Briefly speaking, synthesis of CNTs is done by spray pyrolysis of ferrocene ($C_{10}H_{10}Fe$) and benzene (C_6H_6) solution under Ar at 900°C. In this process, both benzene and ferrocene are used as carbon sources. The CNTs are collected in the powder form. Then, acid treatment of CNTs is done by heating raw CNTs (~80 °C) in concentrated sulphuric acid and nitric acid mixture (taken in the ratio of 3:1) for 8 h. The CNTs are then filtered, washed with deionized water several times to remove the residual acid. Finally, these are dried in an oven at 80 °C for overnight.

Synthesis of graphene-carbon nanotube (Gr-CNTs: GC) composite materials

Graphene and CNTs were mixed with 5 ml of ethanol in separate beakers. Sonication of both solutions was done for 2 h. Both samples were mixed together and sonication of resulting mixture was done for 2 h. Then stirring of sample was done for 6 h with the help of magnetic stirrer (Fig. 1). Finally, sample was dried at 60 °C for 20 h. These graphene-CNTs composite materials were then prepared in the form of a pellet using very small amount of hardener (solution of polyvinyl butyral and polyethylene glycol in ethyl alcohol) under hydraulic pressure (4 tons). The surface morphology of the sample was observed by scanning electron microscope

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