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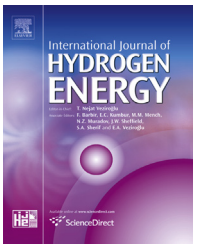

Evaluation of optimum conditions for hydrogen generation in argon-water vapor dielectric barrier discharge

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ABSTRACT

Efficient transformation of water vapor into hydrogen in dielectric barrier discharge in argon medium is reported. Hydrogen in the product gas mixture was identified and estimated by on-line gas chromatography – thermal conductivity detection, with appropriate support of standard hydrogen samples. Experimental parameters varied included reacting gas composition (with respect to water vapor concentrations), its resident time within the plasma zone, nature of surfaces (Pyrex and stainless steel), discharge gas-gap between two surfaces, and in-discharge power consumption. The optimum conditions at applied voltage 7.3 kV @ 50 Hz were: 10,400 ppm water vapor concentration, 12 s gas residence time, in a single pyrex dielectric barrier reactor with 2 mm gas-gap and 13.5 mL gas volume capacity, yielding the maximum hydrogen concentration of 1500 ppm.

Introduction

Hydrogen, primarily derived from water has been claimed to be a good alternative to replace fossil fuels since 1970s. However, the potentiality of hydrogen has not been realized mainly because of storage and commercial production difficulties [1]. Moreover, environment friendly and cost effective processes for efficient production of hydrogen are yet getting developed. Presently UV light [2–5], ionizing radiation [6], sonolysis [7], plasma derived from electrical discharge [8–11] *etc.* are emerging as alternative methods in the context of H_2 generation and its storage besides the large H_2 production from biomass through steam methane reforming process [12]. In this context, H_2 formation from water vapor through plasmolysis has been considered as a potential and cleaner technique [13], wherein ~80% energy efficiency has been reported from steam and water vapor employing dielectric barrier discharge (DBD) – corona hybrid plasma reactor [14]. The principal advantage of the plasma technique was revealed in the high specific productivity, easy access and instantaneous production.

In continuation to the previous work on hydrogen (H_2) and hydrogen peroxide (H_2O_2) yields in argon-water vapor DBD [8], in this study we describe the optimization of various experimental parameters to maximize the on-line H_2 production. Results from this study highlight the need for an optimum level of water vapor in the reaction mixture, as well as its role

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in controlling the H_2 production both as *in situ* and *ex situ* H_2 source in subsequent experimental utilization.

Experimental method

The DBD experimental set-up, with on-line power and product measurement facilities used was same as in our previous work [8], including the arrangement to measure power consumption by Lissajous' plots [15,16]. However, these details are repeated here for easy correlation with the measurements later. In brief, the experimental set-up consisted of a coaxial dielectric barrier reactor, working near atmospheric pressure and room temperature. Four coaxial DBD reactors, two each of single- and double-pyrex dielectric types were used in the study. In the two single-pyrex dielectric (SD) reactors, the inner stainless steel rod diameter in either case was 6 mm and the outer pyrex surface inner diameter was 10 mm. However, the discharge zone lengths were different at 130 mm referred to as SD 10/6S and 270 mm SD 10/6L, with respective gas-volume of 6.5 and 13.5 mL. In the remaining two concentric double-pyrex dielectric (DD) reactors, the outer surface inner diameter was 14 mm in either case, while the inner dielectric outer surface diameters respectively were 10 and 11 mm (referred as DD 14/10 and DD 14/11 combination). With identical discharge zone length of 100 mm, these offered with respective discharge volumes of 7.5 mL (DD 14/10) and 6 mL (DD 14/11). These four different reactors thus offered discharge gas-gaps (GG) of 1.5–2 mm, and discharge volume between 6 and 13.5 mL. In all cases the central electrode was connected to HV power supply, while the top surface of the outer Pyrex tube were silver mirrored and connected to earth. Applied maximum HV was limited to 4.65 kV mm^{-1}. High purity argon (Six Sigma Gases India Pvt Ltd., ≤2 ppm oxygen and moisture) flow was controlled with mass flow controller (MFC). For H_2 detection and estimation gas chromatography – thermal conductivity detector (GC-TCD) (Model: Ceres 800 plus, Thermo Fisher Scientific India Ltd.) with Porapak-Q packed column (0.25 mm ID × 2.4 m) was employed with carrier Ar (flow rate: 15 mL min^{-1}), oven at 45 °C (isotherm), TCD at 220 °C, applied bridge voltage 8.0 V with maximum detector sensitivity. H_2 peak intensities at retention time (R_T) 0.88 min were estimated by comparing with chromatogram of standard H_2–Ar gas mixtures. The error in GC estimations remained within ±5%. In addition to the nature of surfaces in contact with gas (metal and dielectric) various experimental parameters varied were the reacting gas composition (varied water vapor concentration), gas residence time (GRT) within the plasma zone, discharge GG, and electric (in-discharge) power consumed. The water vapor contents in Ar were either increased beyond the existing 2 ppm moisture level to 33, 66 and 100% relative humidity (RH) (corresponds to 10,400, 21,100 and 32,300 ppm by volume [17]) by diverting a known fraction of Ar flowing over water maintained at room temperature (25 °C), or lowered below existing 2 ppm by passing through activated silica gel (a promising trap for water vapor [18,19]). It is important to note at this juncture that the hydrogen production as well as energy dissipation were observed identical in cylinder Ar treated systems both with activated silica gel and subsequent treatment with activated silica gel and molecular sieve 5A (another desiccant [19]) revealing the low moisture concentrations in Ar treated systems. For Lissajous' plots the temporal change of discharge voltage and current were recorded on Tektronix TDS 3052C oscilloscope, and the power consumption inside the DBD reactors were obtained as mW_{total}. For example, the energy dissipation measured with DD 14/10 reactor at 3.1 kV mm^{-1} applied voltage in different water vapor containing systems are compared in Fig. 1 a & b, wherein the Fig. 1a represents the sequential change in voltage and current recorded on oscilloscope during discharge and Fig. 1b depicts the Lissajous' plots. The energy dissipation all these systems were found almost identical (within 10% variation). Similar trends were observed in other reactors.

Results and discussion

We have demonstrated earlier the details about the generation of H_2 and H_2O_2 in moist (100% RH) argon-DBD cold plasma [8]. In continuation, we explored further to optimize hydrogen formation yields, by suitably varying the above-mentioned experimental conditions.

Fig. 2 shows the gas chromatograms of product mixture recorded in different cases using the DD 14/11 reactor before and after plasma discharge along with the chromatogram of standard H_2 sample. The peak obtained with standard sample injection confirmed the peak R_T of 0.88 min was due to H_2. In

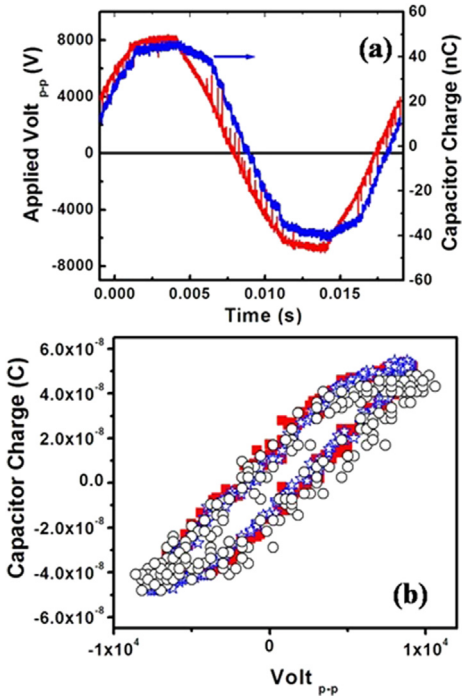

Fig. 1 – (a): The temporal change in voltage and current with time during discharge and (b): Lissajous' plots obtained during energy dissipation measurements (energy per cycle) with DD 14/10 reactor at 3.1 kV mm^{-1} applied voltage with Ar containing ■: <2 ppm moisture ($E_{<2\ ppm}$ 300 μJ); ☆: 2 ppm moisture ($E_{2\ ppm}$ 273 μJ) and ○: 21,100 ppm moisture (66%) ($E_{21100\ ppm}$ 310 μJ).

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