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Short Communication

Low emission hydrogen generation through carbon assisted electrolysis

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ABSTRACT

The conventional electrolysis process for hydrogen generation offers many advantages such as on-site on-demand generation, pure hydrogen that can be stored for latter use directly in fuel cells, and potential of direct coupling to a renewable source of energy. However, the process is very energy intensive. Therefore, at present hydrogen is produced mainly by Natural Gas reforming and coal gasification at temperatures in the vicinity of 800 °C. This method of hydrogen production involves the steps of reforming/gasification, shift reaction and gas separation at high temperatures to improve hydrogen yield and purity based on its application. This paper investigates the thermodynamic and practical energy benefits of single step water electrolysis process assisted by carbon, where part of the energy can come from the chemical energy of carbon. The process has been demonstrated in a solid state electrolytic cell operating at near room temperature. The paper also discusses the technology status and challenges to achieve high hydrogen generation rates.

Introduction

Hydrogen at present is consumed mainly for ammonia and fertiliser production, in oil refineries and methanol and chemical production [1,2]. In future the demand for hydrogen as a clean fuel will grow both for stationary and transport power generation applications. Currently most hydrogen is generated from coal or natural gas with water electrolysis contributing only small percentage points.

Hydrogen production by the electrolysis of water is highly energy intensive process, requiring 6.7–7.3 kW h/Nm^3 of hydrogen in the complete system. The net efficiencies achievable from the commercial electrolysis systems have been reported to be around 50–55% [3]. The use of renewable energy would obviously make it environmentally more sustainable. Moreover if the electrolysis is carried out at higher temperatures the electric energy input per Nm^3 of hydrogen produced can be significantly reduced by embedding solar heat or waste heat from industrial processes or from thermal or nuclear power plants [3]. Furthermore, the electrolysis process can be made more economical if the electrolyser is directly coupled to a renewable source of energy without the extra interfacing electronics as demonstrated previously [4].

Coal will continue to be a major source of power generation for more than a century due to its abundance, however, new methods of its utilisation need to be developed to enhance

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energy conversion efficiency from coal to electricity and/or hydrogen. As opposed to hydrogen production from natural gas or coal, where three separate high temperature process steps (reforming or gasification, shift reaction and H_2/CO_2 separation) are required [5], the carbon assisted electrolysis for hydrogen generation would performs this operation in a single electrochemical reactor with the following reaction steps as described below.

At anode:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \text{ (electrolyte: proton conducting)} \tag{1}$$

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \text{ (electrolyte: } O^{2-} \text{ conducting)} \tag{2}$$

At cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \text{ (electrolyte: proton conducting)} \tag{3}$$

$$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-} \text{ (electrolyte: } O^{2-} \text{ conducting).} \tag{4}$$

The overall reaction is:

$$C + 2H_2O \rightarrow CO_2 + 2H_2. \tag{5}$$

With a solid state electrolyte membrane (polymer electrolyte membrane or solid oxide electrolyte membrane) hydrogen and CO_2 are generated in separate compartments of the cell thus eliminating the costly process of gas separation. For conventional coal fired power plants, nearly 25% energy is lost in CO_2 capture in addition to the substantial cost of CO_2 capture. The source of carbon can be low grade coal (brown coal) or biomass. There will be some costs associated with pretreatment of the carbon fuel such as pulverisation for making carbon-water slurries, however, such costs are expected to be similar or only marginally higher than those for coal preparation for thermal power stations. Further, the cost of coal and its preparation will be well compensated by the lowering of the power input required for electrolysis due to the chemical energy input from coal as discussed latter in the paper. All these benefits would directly translate into a highly efficient process with low overall cost and substantially reduced CO_2 emissions.

Despite the many advantages the carbon electrolysis process offers for hydrogen generation, there has been little effort so far in developing the technology. Previous studies have been performed mainly using aqueous electrolyte systems (H_2SO_4, H_3PO_4, NaOH), either using a single compartment electrolysis cell or by using a separator (glassy fibre or proton conducting membrane) between the anode and cathode chambers [6–10]. Coal slurries were prepared using carbon sources such as Pittsburgh coal, lignite, activated charcoal and char in the tens of microns size range. The noble metal catalysts (Pt, Pt–Rh, Pt–Ru, Pt–Ir), deposited on a substrate such as titanium sheet or mesh, were used for the electrolysis process. Very low current densities of less than 10 mA/cm^2 at cell operating temperature of up to 114 °C were reported. However, by the addition of Fe^{2+}/Fe^{3+} ionic species (in the form of iron sulphate salts), higher current densities in the tens of mA/cm^2 range have been achieved [9,10].

The use of polymer electrolyte membrane cells, where not only the carbon assisted electrolysis can be carried out at low temperatures but would also allow production of hydrogen and CO_2 in separate compartments of the electrochemical cell for easy capture and storage of CO_2. This novel concept is largely unexplored with very little global effort. In this paper, through thermodynamics and energy balance calculations, we have shown the advantages of the carbon assisted electrolysis to produce hydrogen. Furthermore, preliminary experiments have been performed to demonstrate the feasibility of carbon assisted hydrogen production in a polymer electrolyte membrane cell.

Process thermodynamics and energy balance

Fig. 1 shows the thermodynamics of the carbon assisted electrolysis process at low to intermediate temperatures [6]. The reversible thermodynamic voltage of the cell in this case is 0.21 V at 20 °C (1 atm pressure) compared to 1.23 V for conventional electrolysis. The electrolysis process begins only above thermo-neutral cell voltage, which is 0.45 V and 1.48 V respectively for carbon assisted and conventional electrolysis. Therefore, due to the electrochemical involvement of carbon in the reaction, the electrolysis process would potentially require about 1/3rd the electrical energy with the balance of 2/3rd coming from the chemical energy of carbon in comparison with conventional water electrolysis where all the energy input is electric. Fig. 2(a) shows the cell voltage and percentage electric energy savings from a carbon assisted electrolyser

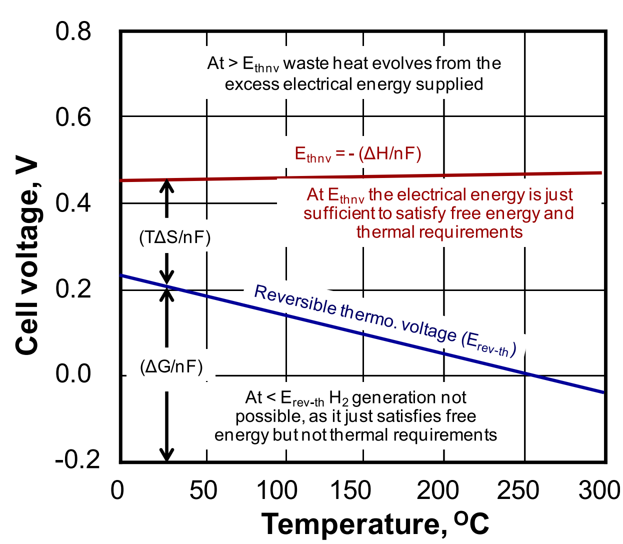

Fig. 1 – Thermodynamics of the carbon assisted electrolysis process showing the dependency of reversible and thermo-neutral voltage on cell temperature. (Figure is redrawn from Ref. [6]).