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Pulsed current water splitting electrochemical cycle for hydrogen production

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ARTICLE INFO

Article history:

Received 11 December 2017

Received in revised form

21 March 2018

Accepted 11 April 2018

Available online xxx

Keywords:

Water splitting

Pulsed current

Hydrogen evolution reaction

Oxygen evolution reaction

ABSTRACT

A pulsed current 3 D MnO₂ electrode water splitting electrochemical cycle is being proposed for hydrogen production. In 3D MnO₂ electrochemical cycle, the reactions take place at the solid/liquid and solid/gas two phase boundaries. Also, this electrochemical cycle should be able to generate hydrogen and oxygen gas separately at different periods of time. Here, we applied an interrupted pulsed current to reduce the overpotential caused by diffusion layers in conventional direct current electrolysis. The pulsed current, which disturbs the formation of the ion diffusion layer in the vicinity of the electrodes, is observed to be effective above 50 Hz. The best electrolysis performance was recorded at a current density of 0.2 A cm⁻², and the observed cell voltage was 1.69 V at 25 °C for a pulse frequency of 500 Hz, which is less than the corresponding conventional alkaline electrolysis.

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Introduction

Hydrogen is one of the most promising energy carriers for domestic and industrial energy systems [1]. In general, hydrogen is produced by the reforming of natural gas [2]. This process causes a depletion of fossil energy and an increase of CO₂ emission. Recently, hydrogen production by water electrolysis using renewable energy, such as solar, wind power, and photovoltaics, has received much attention [3]. Alkaline and proton exchange membrane (PEM) electrolysis are the two major types of low temperature water electrolysis. These technologies have the capacity to obtain pure (99.999%) and

pressurized hydrogen [4]. Proton exchange membrane electrolysis demands the choice of a suitable catalyst material from the noble metals, which contributes to the higher investment costs (1900–2300 €/kW) [5,6]. Alternatively, alkaline electrolysis is a mature technology and has been widely used in industrial hydrogen production [7]. The major advantage of alkaline water electrolysis is the low investment cost (1000–1200 €/kW) because of the non-noble metal catalysts and less expensive separators [8–11]. However, a large overpotential is associated with alkaline electrolysis. Hence, there has been considerable interest to develop novel electrodes and to modify alkaline electrolysis, which has predominantly focused on low cost, high performance, and stability.

Nomenclature: δ_s , stationary layer; δ_p , pulsating electro dynamic diffusion layer; t_p , pulse-time; D , diffusion co-efficient.

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<https://doi.org/10.1016/j.ijhydene.2018.04.087>

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Recently, a 3D metal hydride (MH) particle electrode was introduced as a negative electrode for the hydrogen production and power generation system to reduce the overpotential [12] [13]. In 3D particle electrodes, the reactions take place at the solid/liquid and solid/gas two phase boundaries. This leads to suppression of the overpotential because of an increase in the reactive area. The achieved conversion efficiency of hydrogen production and power generation were 98.3 and 79.6% at 37 A m⁻². In our previous study, a novel water electrolysis system containing an intermediate electrode was presented, which could generate oxygen and hydrogen gases separately through two electrochemical cycles [14]. This water splitting electrochemical cycle system can achieve a high energy conversion efficiency during hydrogen production by reducing the ohmic overpotential between the electrodes through the use of a thinner separator than that used in conventional systems. In this water splitting electrochemical cycle, hydrogen is generated by applying a voltage between the negative and intermediate electrodes. However, by applying a voltage between the intermediate and positive electrodes, oxygen is evolved at the surface of the positive electrodes. By using this water splitting electrochemical cycle, the overall cell voltage was reduced to 1.78 V for a current density of 5 mA cm⁻² at 25 °C.

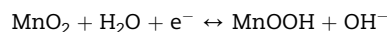
L. Chen et al. [24], recently tested an alkaline water electrolytic cell with Ni(OH)₂ intermediate electrode, constructed with a commercial Pt-coated Ti-mesh electrode and commercial RuO₂/IrO₂-coated Ti-mesh electrode for HER and OER electrodes. The water electrolysis of the cell was investigated by chronopotentiometry measurements with different applied currents of 0.02 A cm⁻² and the resulting cell voltage was around 2 V.

In conventional DC power electrolysis, the formation of an ion diffusion layer takes place near the surface of the electrodes. Hence, DC electrolysis is an ion diffusion limited process that leads to a large overpotential. Recent studies have shown that an interrupted power supply may disturb the formation of the ion diffusion layer near the surface of the electrodes [15,16]. This can reduce the concentration overpotential tending to the destruction of the ion diffusion layer [17]. In the present work, we have introduced pulsed current to the 3D MnO₂ water splitting electrochemical cycle to reduce the concentration potential resulting from conventional DC power supply. We have examined the effect of frequency on the performance of the electrolyzer.

Theory

Water splitting electrochemical cycle with an 3D MnO₂ intermediate electrode

Manganese dioxide is one of the candidates for electrode material, which has high electrochemical capacity (theoretical capacity: 308 mAh/g per one electron reaction), and relatively low price shows promise as an intermediate electrode. The redox reaction and redox potential (relative to the standard hydrogen electrode; SHE) for manganese dioxide can be represented as follows:



$$E = E^0 - (2.303RT) \times \text{pH} = 0.977 - 0.0591 \times \text{pH} (T = 298.15\text{K})$$

where T (K) and R (=8.314 J mol⁻¹ K⁻¹) are the temperature and gas constant, respectively. E⁰ and E are the standard redox potential and redox potential at the pH and temperature of interest, respectively. In a strongly alkaline solution (pH 14), the redox potential for manganese dioxide is 0.15 V, which is below the potential for oxygen evolution reaction (0.402 V vs SHE) and above the potential for the hydrogen evolution reaction (-0.828 V vs SHE).

The two-step electrochemical cycle system is composed of three electrode materials in an alkaline solution: (i) MH as the negative electrode; (ii) manganese dioxide (MnO₂) as the intermediate electrode; and (iii) nickel hydroxide (Ni(OH)₂) as the positive electrode, as shown in Fig. 1. This cycle is comprised of two different cycles, which are the hydrogen evolution cycle and oxygen evolution cycle. In the hydrogen evolution cycle, hydrogen is produced by reduction of water at the negative electrode and oxidation of MnO₂ to MnOOH occurs at the intermediate electrode. In the oxygen evolution cycle, oxygen is produced by the reduction of MnOOH to MnO₂ at the intermediate electrode and OH⁻ oxidation occurs at the positive electrode. This process takes place continuously for a given period of time. The reaction mechanism in the proposed alkaline water electrolysis system based on nickel–metal hydride (NiMH) batteries: with a manganese dioxide electrode as an intermediate electrode, respectively. The two electrochemical cycle reactions are shown in Fig. 2.

The calculated thermodynamic data, enthalpy and Gibbs free energy changes in water electrolysis, and the electrochemical water splitting reactions are summarized in Table 1. The electrochemical cell voltage of the two cycles can be calculated using the equation $\Delta_rG = -nFE$, where Δ_rG , n, F, and E are the change in Gibbs free energy (kJ/mol) during reaction, the number of electrons per mole of product, the Faraday constant (96,485.3 C/mol), and the cell voltage of the reaction (V). From Table 1, the cell voltage for water electrolysis (1.229 V) is divided into 0.145 V for oxygen generation and 1.084 V for hydrogen generation.

Material and methods

Preparation of electrodes

The positive electrode was prepared from a homogeneous solution consisting of Ni(OH)₂, carbon black (CB) and ethylene–vinyl acetate (EVA) with a mass ratio of 100:1:3. The particle diameter of the NiOH particles was 0.5–1.7 μm. A nickel foam support was dipped in the solution then rolled up to a thickness of 0.5 mm followed by pressing at 30 MPa for 5 min.

The negative electrode was fabricated by the slurry method. The slurry was prepared by mixing of lanthanum, Ni carbon black and ethylene vinyl acetate. The mass ratio of the slurry was 100:5:5. The slurry was heated at 120 °C for 30 min to dissolve the EVA in xylene. The slurry was then mixed well and cooled until the mixture became a solid. The solidified mixture was ground and sieved to obtain particles around

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