A concise model for evaluating water electrolysis

Muzhong Shen [a,*], Nick Bennett [a], Yulong Ding [b], Keith Scott [c]

[a] Department of Mechanical & Design Engineering, University of Portsmouth, Portsmouth PO1 3DJ, UK
[b] School of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, UK
[c] School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

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ABSTRACT

To evaluate water electrolysis in hydrogen production, a concise model was developed to analyze the current–voltage characteristics of an electrolytic cell. This model describes the water electrolysis capability by means of incorporating thermodynamic, kinetic and electrical resistance effects. These three effects are quantitatively expressed with three main parameters; the thermodynamic parameter which is the water dissociation potential; the kinetic parameter which reflects the overall electrochemical kinetic effect of both electrodes in the electrolytic cell, and the ohmic parameter which reflects the total resistance of the electrolytic cell. Using the model, different electrolytic cells with various operating conditions can be conveniently compared with each other. The modeling results are found to agree well with experimental data and previous published work.

1. Introduction

Hydrogen is a clean fuel for fuel cell applications. Combined with solar cell systems or wind power systems, hydrogen produced with water electrolysis will play an important role as an energy carrier for sustainable development in future [1]. For reducing operating costs and increasing energy efficiency, there are many techniques and research works [2–9] concerning the water electrolysis process. Compared with traditional alkaline electrolysis [4], in which corrosive potassium hydroxide (KOH) solution is used as the electrolyte, proton exchange membrane (PEM) electrolysis has acquired a lot of attention for its advantages of ecological cleanliness, high degree of hydrogen purity, and easy maintenance [10]. In general, all these research works try to improve the electrolysis performance from two aspects; to increase electrochemical activity of electrodes and to reduce the total resistance of the electrolytic cell.

The water electrolysis performance is normally evaluated with the current–voltage characteristics of an electrolytic cell as shown in Fig. 1. Several models [11–13] have been developed to try to simply and effectively simulate the current–voltage characteristics of PEM electrolysis for hydrogen production. With present models, the cell voltage is basically described as the sum of Nernst voltage, resistive voltage drop, and anode and cathode overpotentials [14]. The anode and cathode overpotentials are usually obtained via the Butler–Volmer kinetic equation. To solve the Butler–Volmer equation, two parameters of exchange current density for the anode and the cathode are required to describe the electrode activities. Additionally, the symmetrical factors of the equation also need to be assumed as a specific number [15]. The exchange current density depends on the temperature and the roughness of the electrode surface [13]. In most case, the values of exchange current density for anode and cathode are

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* Corresponding author.
  E-mail address: muzhong.shen@port.ac.uk (M. Shen).

different to each other [11,12]. All these make it difficult to predict the water electrolysis performance directly.

In this paper, a new model is proposed to simulate the current–voltage characteristics of water electrolysis. The water electrolysis capability of an electrolytic cell was expressed through three main parameters which reflect the thermodynamic effect, the overall electrochemical kinetic effect and the total resistance of the electrolytic cell. With these parameters, different electrolytic cells in various operating conditions can be conveniently compared with each other. An experiment was designed to investigate the water electrolysis process with different electrode materials and cell resistances. The modeling results are compared and validated with the experimental data and with previously published work.

2. Model description

2.1. The fundamentals of water electrolysis

Water electrolysis is the process of dissociating water molecules into hydrogen and oxygen gas using electrical power. The electrochemical reaction happens on both anode and cathode.

At the anode:

$$H_2O(l) \Leftrightarrow 2H^+ + \frac{1}{2}O_2 + 2e \quad E_{anode}^0\,(25°C) = 1.23\,V \tag{1}$$
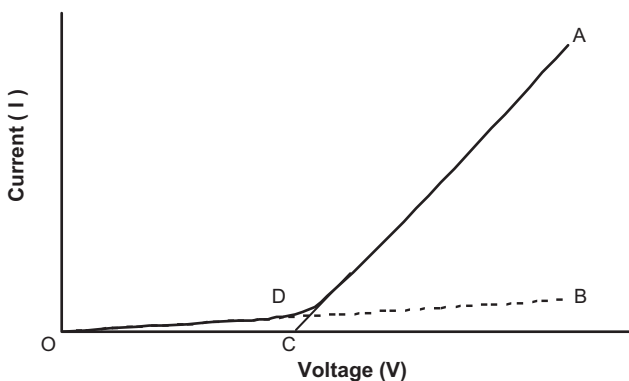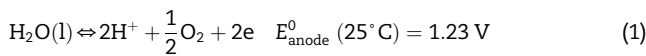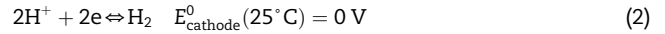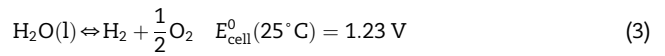

Fig. 1 – The relationship between the current versus potential of water electrolysis.

At cathode:

$$2H^+ + 2e \Leftrightarrow H_2 \quad E_{cathode}^0(25°C) = 0\,V \tag{2}$$

The net reaction in the electrolytic cell is:

$$H_2O(l) \Leftrightarrow H_2 + \frac{1}{2}O_2 \quad E_{cell}^0(25°C) = 1.23\,V \tag{3}$$

The reversible potential reflects the thermodynamic effect of electrochemical reaction. The Nernst equation of water electrolysis is shown as equation (4) [16].

$$E_{cell}^0 = 1.23 - 0.9 \times 10^{-3}(T - 298) + \frac{RT}{4F}\ln\left(\frac{p_{H_2}^2 \cdot p_{O_2}}{p_{H_2O}}\right) \tag{4}$$

where p_{H_2}, p_{O_2} and p_{H_2O} are the partial pressures of hydrogen, oxygen and water vapor respectively. Although the reversible potential of water electrolysis at 25 °C is 1.23 V, the water dissociation potential is influenced by the catalyst activity of electrodes. When platinum is used as the anode and cathode, the dissociation potential is 1.68 V [9]. The dissociation potential can be reduced to 1.4 V when platinum and iridium are used as electrocatalysts [2,6,9,17]. The electrochemical properties of electrodes not only influence the kinetic effects of water electrolysis, but also influence the mechanism of electrochemical reaction which decides the value of water dissociation potential.

The kinetic effect of water electrolysis is conventionally expressed with the Butler–Volmer equation via the activation overpotential of both electrodes which can be expressed as equation (5) [12].

$$\eta_{act,i} = \frac{RT}{F}\sinh^{-1}\left(\frac{J}{2J_{0,i}}\right) = \frac{RT}{F}\ln\left[\frac{J}{2J_{0,i}} + \sqrt{\left(\frac{J}{2J_{0,i}}\right)^2 + 1}\right], \quad i = a,\,c \tag{5}$$

where $\eta_{act,i}$ is the activation overpotential and subscripts a and c represent anode and cathode respectively; J is the operating current density; $J_{0,i}$ is the exchange current density. The exchange current density can be expressed as equation (6).

$$J_{0,i} = J_i^{ref}\exp\left(\frac{E_{act,i}}{RT}\right), \quad i = a,\,c \tag{6}$$