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Alkaline electrolysis cell at high temperature and pressure of 250 °C and 42 bar

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HIGHLIGHTS

- ► A new type of an alkaline electrolysis cells has been developed.
- ► Metal foam based gas diffusion electrodes with Ag electro-catalyst were used.
- ► Potassium hydroxide as electrolyte was immobilized in a porous $SrTiO_3$ structure.
- ► The cells have shown to operate at temperatures up to 250 °C at 42 bar.
- ► Current densities of 1.0 A cm^{-2} and 2.0 A cm^{-2} have been measured at 1.5 V and 1.75 V.

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ABSTRACT

A new type of alkaline electrolysis cells with nickel foam based gas diffusion electrodes and KOH (aq) immobilized in mesoporous $SrTiO_3$ has been developed and tested at temperatures and pressures up to 250 °C and 42 bar, respectively. Current densities of 1.0 A cm^{-2} have been measured at a cell voltage of 1.5 V without the use of expensive noble metal catalysts. High electrical efficiency and current density combined with relatively small production costs may lead to both reduced investment and operating costs for hydrogen and oxygen production.

1. Introduction

Energy from renewable sources is becoming an increasingly important part of the energy supply system worldwide. Besides the obvious advantages of renewable energy sources, like CO_2 free or neutral energy production, some indisputable disadvantages have to be overcome towards a sustainable energy supply system [1]. The fluctuation of the wind speed and solar radiation, for example, leads to periods with excess or deficit of available energy. It is therefore necessary to develop energy storage systems with high efficiency and reliability, as well as low cost. The production of hydrogen by means of electrolysis of water during times of energy excess, followed by conversion of the produced hydrogen to electricity during periods of energy deficit is a promising possibility [2]. Alkaline electrolysis has proven to be reliable and efficient some decades ago [3], but further cost reduction along with increased efficiency is still necessary in order to make it commercially attractive. A significant reduction of the investment costs may be achieved by increasing the operational pressure of the electrolyzer as this will result in the production of pressurized hydrogen (and oxygen), thereby eliminating or reducing the cost of the compressor. Furthermore, it has been estimated that the energy demand for pressurization by the electrolyzer is ca. 5% less than for pressurization by common compressors, leading to reduced operation cost for the system [4].

A substantial step towards higher efficiencies can be made by increasing the operational temperature from the conventionally used temperature of about 100 °C to temperatures as high as 264 °C, where a current density of 200 mA cm^{-2} has been demonstrated at a cell voltage of 1.43 V [5]. Another substantial step forward has been made by Divisek et al. by the use of Raney activated electrodes and zero-gap electrodes, thereby achieving a current density of 400 mA cm^{-2} at a cell voltage of ca. 1.55 V at 100 °C and pressures between 1 and 5 bar [3].

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1.1. Alkaline electrolysis

An alkaline electrolysis cell consists of four major components; the electrolyte, which is commonly potassium hydroxide (KOH) in high concentrations (usually above 25 wt%), the cathode, the anode, and a solid barrier (diaphragm). The solid barrier is separating the produced gases to avoid recombination and furthermore needs to be permeable to hydroxide ions and water; it is used in all types of alkaline electrolysis cells (conventional, zero-gap, immersed cells, or gas diffusion electrode type alkaline electrolyzers) [6,7]. Hydrogen evolution takes place at the cathode, where the electrons are provided for the decomposition of water. The hydroxide ions are decomposed at the anode, where oxygen evolution takes place under the formation of water. The basic reactions of the decomposition of water in an alkaline electrolyzer are given by Equations (1)–(3).

$$\text{Anode}: 2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \tag{1}$$

$$\text{Cathode}: 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

$$\text{Total}: H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{3}$$

The cell voltage, U_{cell}, that has to be applied to produce hydrogen and oxygen with a given rate depends on the operating temperature [8] and pressure [4] as well as on a number of other factors such as the electro-catalyst material and microstructure [9]. Furthermore, the right choice of electrolyte concentration for a specific temperature [10], and a high specific surface area of the electrodes are important factors. Major losses are defined as cathodic overvoltage, η_{H_2}, for the hydrogen evolution reaction, HER, the anodic overvoltage, η_{O_2}, for the oxygen evolution reaction, OER, and ohmic losses in the electrolyte. The ohmic losses are relatively small at low current densities, but become significant at industrially relevant current densities of 200 mA cm^{-2} or more, especially if significant bubble formation takes place [11].

1.2. Thermodynamic considerations

The reversible (or equilibrium) cell voltage, E_{rev}, is the minimal voltage at which electrolysis of H_2O is possible and can be calculated by equation, where ΔG_f is the Gibbs free energy of the reaction, n is the number of electrons involved in the reaction, and F is Faraday's constant (96,485 C mol^{-1}). At standard conditions it is 1.229 V with the Gibbs free energy of formation at standard conditions $\Delta G_f^0 = -237.178$ kJ mol^{-1} [12].

$$E_{\text{rev}} = \frac{-\Delta G_f}{nF} \tag{4}$$

The total energy demand for the reaction corresponds to the thermoneutral voltage, E_{tn}, and can be calculated from the enthalpy of formation, ΔH_f, as shown by Equation (5). The thermoneutral voltage $E_{\text{tn},0}$ at standard temperature and pressure (STP, 25 °C, 101.325 kPa) is 1.481 V with the standard enthalpy of formation $\Delta H_f^0 = -285.840$ kJ mol^{-1} [12].

$$E_{\text{tn}} = \frac{-\Delta H_f}{nF} \tag{5}$$

A comparison of the electrical energy demand, the total energy demand and the heat demand for water electrolysis at standard pressure is shown in Fig. 1 with thermodynamic data obtained from FactSage [12]. It is shown that the electrical energy demand for water electrolysis decreases with increasing temperature, while heat demand rises and the total energy demand is almost constant (but different) both for the liquid and the gaseous phase.

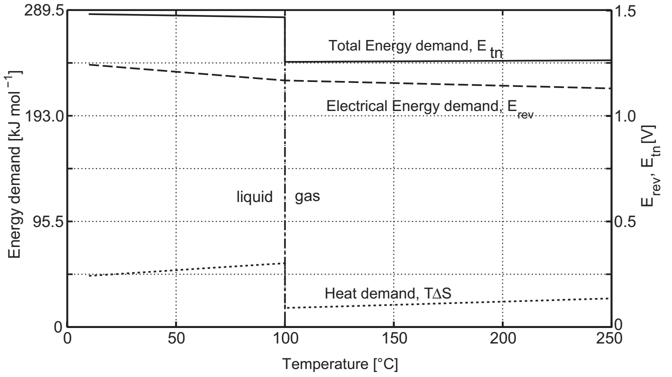

Fig. 1. Temperature dependence of the total energy demand, ΔH_f (full line), the electrical energy demand, ΔG_f (dashed line), and the heat demand $T\cdot\Delta S_f$ (dotted) for water ($T \leq 100$ °C) and steam ($T \geq 100$ °C) electrolysis at 1 bar using data from FactSage [12].

As it is not common to perform electrolysis at standard conditions, it is necessary to know both the influence of pressure and temperature to the reversible cell voltage. The reversible cell voltage as a function of temperature and pressure, $E_{\text{rev}(t,p)}$, can be calculated by Equation (6), where R is the Gas constant (8.3144621 J mol^{-1} K^{-1}), a_{H_2} is the hydrogen activity, a_{O_2} is the oxygen activity, a_{H_2O} is the activity of water and T is the temperature in Kelvin.

$$E_{\text{rev}(t,p)} = \frac{-\Delta G_f}{n\cdot F} = \frac{-\Delta G_f^0}{n\cdot F} + \frac{RT}{nF}\ln\left(\frac{a_{H_2}a_{O_2}^{\frac{1}{2}}}{a_{H_2O}}\right) \tag{6}$$

$E_{\text{rev}(t,p)}$ can also be obtained from steam tables or CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) programs like FactSage [12] which include data for ΔG_f at elevated temperatures and pressures. A graph displaying the influence of the pressure and temperature to $E_{\text{rev}(t,p)}$ has been calculated by Equation (4) with data from FactSage and is shown in Fig. 2 (the partial pressure of H_2, O_2 and H_2O is assumed equal to the total pressure in this calculation). Important values are numerically extracted in

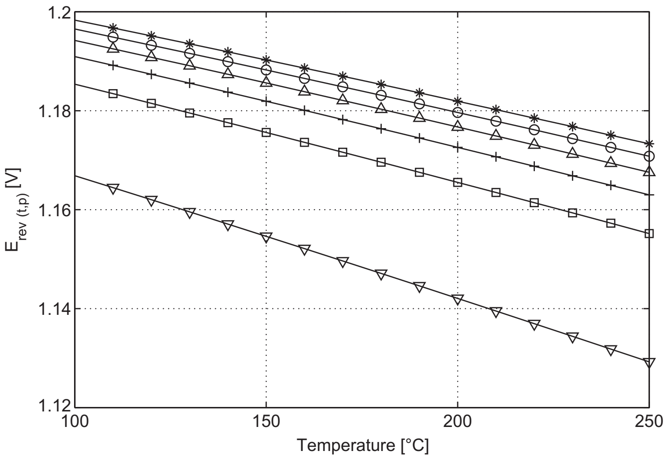

Fig. 2. Reversible cell voltage $E_{\text{rev}(t,p)}$ as a function of the temperature for steam electrolysis at pressures of 1 bar (∇), 10 bar (□), 20 bar (+), 30 bar (△), 40 bar (○) and 50 bar (★) (the partial pressure of H_2, O_2 and H_2O is assumed equal to the total pressure in this calculation).