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Dynamic Model of Chloralkali Membrane Process

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Abstract

Chloralkali is one of the most important and energy intensive processes in the chemical industry. The process produces chlorine through electrochemical conversion. The process's energy consumption is a major production cost for the chloralkali industry. Since the demand for energy efficiency and environmentally friendly processes in industry increases, ion exchange membranes are used intensively in the process. One of the prospective energy sources for this process is renewable energy, which shows strong fluctuations and highly unpredictable behavior. Dynamic behavior of the process becomes important to measure and predict the feasibility of the process. Therefore, modelling of the process dynamics is required. Rigorous model of material balance and voltage balance of the process are developed and investigated in this paper. The material transport phenomena inside the electrolyser are modelled considering a number of driving forces. The developed model also predicts the voltage and current density of the cell. The process simulation result is compared to experimental data.

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1. Introduction

By now, renewable energy has become an important component of Germany's energy mix. In 2014, renewable sources amounted to 26.2% of power generation, and this is increasing further due to the German Government requiring the renewable energy share in power generation to reach 40 - 45% by 2025 and 55 - 60% by 2035 [14]. The anourmous share of renewable energy introduces its dynamic characteristics into the whole power grid. An integration with energy storage systems is one of the possible solutions for fluctuating power generation. Unfortunately, the power generation has reached the limit of energy storage's capacity and the produced electricity needs to be consumed in order to save the integrity of the power grid. This condition causes electricity prices to fall below zero. Another possible solution for the overproduction of electricity is a demand response scheme. The chemical industry emerges as one of the potential energy consumers for the latter. Chlorine is one of the most indispensable intermediates in the chemical industry. It is commonly produced through the chloralkali process, which is an electrochemical process that decomposes an aqueous solution of sodium chloride by direct current, producing chlorine gas, hydrogen gas, and sodium hydroxide solution. The process' energy consumption dominates the production costs. Given the large-scale introduction of renewable energy sources in Germany's electrical grid, both energy suppliers as well as consumers must adjust to an increasingly flexible market. Therefore, dynamic operation of the process has become a new issue in recent discussions.

In a previous paper [17], the dynamic characteristic of a chloralkali process has been modelled. The model assumed that the driving force for ion diffusion through the membrane is just the concentration gradient. Toshikatsu Sata [18] explained the significance of the electric potential gradient as an additional driving force of the ionic transport through the ion exchange membrane. In this paper, the process model includes the electric potential as a major driving force for ion transport through the

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membrane. The model is compared with experimental data from reference [4]. The dynamic behavior of the chloralkali process is simulated in order to understand the dynamic response of the chloralkali process to an increase of the current density.

2. The Process Model

The chloralkali process consists of two half-cells, which are known as anode cell and cathode cell. In the anode cell, oxidation of chloride ions takes place. And electrons are driven towards the cathode by an external electric potential. Within the cathode cell, the transferred electrons reduce hydronium ions. The chemical reactions, which are considered in the developed model, can be expressed as:

Anode cell: $2Na^+ + 2Cl^- \rightarrow Cl_2 + 2Na^+ + 2e^-$
$2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode cell: $2H_2O + 2e^- \rightarrow H_{2(g)} + OH^-$
$Na^+ + OH^- \rightarrow NaOH_{(aq)}$

Total reaction: $2H_2O + 2NaCl \rightarrow H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$

The developed model consists of material balances for all ions, liquids and gases and the energy balance in terms of voltage in the electrochemical cell. Figure 1 illustrates the process, which is modelled in this study.

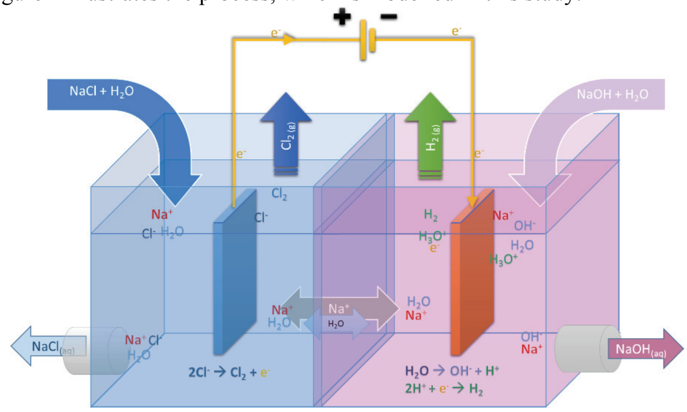

Fig. 1 Diagram of chlor-alkali model

The reactor was modelled as a continuously stirred tank reactor, which makes the electrolyte concentration uniform in each cell compartment. The material balance considers sodium ions, hydroxide ions, water, and chloride. The liquid volume of each half cell is assumed to be constant. Based on Faraday's Law, redox reaction rates in the chlor-alkali cell are estimated with the following expressions:

[redacted] (1)

[redacted] (2)

wherein $\dot{N}$ is the molar rate of production in kmol/s, and subscript *CatOut* and *AnOut* denote cathode outlet and anode outlet respectively. The model assumes that the current efficiency is 100%, so that the quantity of produced gas flows out of both compartments is equal to the production rate of the gases. The other parallel reactions, which appear to be current inefficiencies, are neglected in this model. Tilak and Chen [2] mention that chlorine gas in the anode might dissolve in water to form soluble chlorine, which hydrolyses to form HOCl and OCl^-. Both of them react further to form ClO_3^-. However, based on reference [3], the solubility of Chlorine in water and a solution of NaCl is below 1% of the solution weight when the solution temperature is above 20 ^oC. In accordance with [3], Fig. 2 shows that the solubility of chlorine in water, HCl solution, and NaCl solution decreases with rising temperature and concentration. Hence, the influence of these parallel reactions is minor compared to the other chloralkali reactions, and can be neglected.