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Review (Special Column on Electrocatalysis for Fuel Cells)

A review of the development of high temperature proton exchange membrane fuel cells

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ABSTRACT

Due to the need for clean energy, the development of an efficient fuel cell technology for electricity generation has received considerable attention. Much of the current research efforts have investigated the materials for and process development of fuel cells, including the optimization and simplification of the fuel cell components, and the modeling of the fuel cell systems to reduce their cost and improve their performance, durability and reliability to enable them to compete with the conventional combustion engine. A high temperature proton exchange membrane fuel cell (HT-PEMFC) is an interesting alternative to conventional PEMFCs as it is able to mitigate CO poisoning and water management problems. Although the HT-PEMFC has many attractive features, it also possesses many limitations and presents several challenges to its widespread commercialization. In this review, the trends of HT-PEMFC research and development with respect to electrochemistry, membrane, modeling, fuel options, and system design were presented.

1. Introduction

A proton exchange membrane fuel cell (PEMFC) offers the highest energy density among the many types of fuel cells. Due to its low temperature operation between 60 to 80 °C, PEMFCs can start quickly and provide good responses to changes in power demand [1,2]. Other advantages of the PEMFCs include their low weight and volume and high power density. These advantages of the PEMFCs make them promising candidates for applications in transportation and in portable and small stationary applications. However, there are several difficulties in the operation of a PEMFC that still need to be resolved. The intrinsic problems of PEMFCs are water management and CO poisoning. Due to the proton conduction mechanism in the membrane electrolyte in PEMFCs, the fuel stream must be humidified to avoid the loss of PEMFC performance by membrane dehydration. The liquid water generated at the cathode catalyst layer from the electrochemical reaction and the proton conduction mechanism (electro-osmotic drag) causes a water flooding problem. In addition, trace CO in the hydrogen-rich gas can strongly adsorb on the surface of Pt and block the hydrogen oxidation reaction (HOR) sites. This will dramatically reduce the activity of Pt or Pt alloy in the anode, which results in the deterioration of PEMFC performance.

Recently, a high temperature PEMFC (HT-PEMFC) operated between 100 and 200 °C was developed. The operation of the PEMFC at high temperature reduced the CO poisoning problem and gave it a high tolerance for CO. Therefore, the high temperature operation of PEMFCs can improve the PEMFC performance when it is operated with a reformate gas. Another ad-

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vantage of the HT-PEMFC is that the electrochemical reaction rates at the anode and cathode are increased and water management within the PEMFC is simplified. In addition, the released heat from the HT-PEMFC can be applied for hydrogen production and a co-generation system.

This review focuses on the development of the HT-PEMFCs reported in the literature. The basic operation and principle of the HT-PEMFC are explained. The development of proton exchange membranes for high temperature operation is summarized. Since several types of fuels, including hydrogen, reformate gas and methanol, can be used in the operation of HT-PEMFCs, the effects of the fuel on the performance of the HT-PEMFC are discussed. A description of the electrochemistry involved in the oxidation of hydrogen and the reduction of oxygen is given in terms of the limitations and the approaches to overcome the limitations of the reactions. The various models of the HT-PEMFCs in the literature are reviewed to understand the design and control of complex PEMFCs. The trends in the integration of the HT-PEMFC process with a fuel processor and the heat and power systems are considered. The heat integration between the hydrogen production process and the other heat requirement systems in the HT-PEMFCs are also discussed.

2. Principle and theory of HT-PEMFCs

The HT-PEMFC is a promising PEMFC technology that was developed to solve the main problems of a conventional, low temperature PEMFC (LT-PEMFC), namely, CO poisoning of the Pt catalyst and water management in both the gas diffusion layer and the membrane. Compared to the LT-PEMFC, which is operated between 60 to 80 °C, the HT-PEMFC provides a higher power efficiency and a wider range of thermal energy usage. The HT-PEMFC is operated at high temperatures between 100 to 200 °C. Under the high temperature operation, the amount of CO that adsorbs on the Pt catalyst in the HT-PEMFC is reduced, which results in a high CO tolerance. Therefore, the operation of the PEMFC at high temperature can mitigate the CO poisoning problem. In addition, the higher operating temperature of the PEMFC also increases the electrochemical reaction rates at the anode and cathode and simplifies water management in the PEMFC. When the PEMFC is operated at temperatures above 100 °C, water is only present in the vapor phase and thus the flooding problem is solved and the transport of water is easily balanced. However, the operation of the PEMFC at high temperature leads to the dehydration of the membrane and the loss of the membrane's ionic conductivity. The development of novel membranes that can be operated at temperatures higher than 100 °C and that exhibits high conductivity under a low humidity is a critical issue.

Basically, the HT-PEMFC structure is similar to a conventional PEMFC. Both consists of a polymeric proton-conductive membrane sandwiched between an anode and a cathode backing layer (or gas diffusion layer, GDL), as shown in Fig. 1, but they differ in the type of membrane utilized. The electrodes must be porous so that the gaseous reactants can diffuse to the interface between the electrodes and the membrane to the

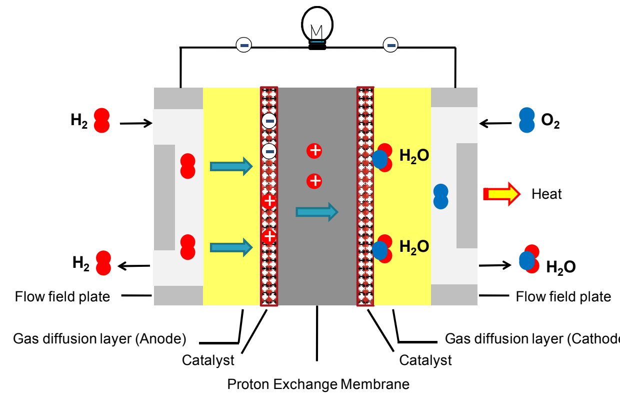

Fig. 1. Schematic of an HT- PEMFC.

surface of the catalyst layer where the electrochemical reactions take place. During the operation of the HT-PEMFC, hydrogen is fed into the anode side without humidification where it is dissociated into its primary constituents, protons and electrons, (Eq. (1)), at the catalyst (Pt) layer. The protons subsequently migrate through the membrane from the anode to the cathode side, while the electrons go through the electrically conductive electrodes to the outside circuit and return to the cathode. At the cathode, the electrons react with the protons from the anode side and with the oxygen (Eq. (2)). Water is produced in this electrochemical reaction and is removed from the cell by a flow of excess oxygen.

$$\text{Anode: } 2H_2 \rightarrow 4H^+ + 4e^- \quad (1)$$

$$\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

Due to the high CO tolerance of the HT-PEMFC compared to the conventional PEMFC, a reformate gas can be used as fuel without complex CO removal processes. This makes the design of the fuel processor for the HT-PEMFC simpler. The typical HT-PEMFC system is presented in Fig. 2(a). It does not have any of the variety of CO removal approaches, such as the preferential oxidation process, pressure swing adsorption, CO methanation process or process involving a membrane separation and humidifier, that is required for the conventional PEMFC system, which are shown in Fig. 2(b).

3. Proton exchange membrane for HT-PEMFC

Apart from the operating temperature, the main difference between the conventional PEMFC and HT-PEMFC is the type of proton exchange membrane. The well-known membrane material for the PEMFC is Nafion™, which is made of a perfluorocarbon-sulfonic acid ionomer. The fuel needs to be saturated with steam before it is fed to cell from the anode side to prevent the drying out of the Nafion membrane. This is because the proton transport mechanism (vehicle or hopping mechanism) across this membrane uses water as a proton carrier. Although the operation of the PEMFC at an elevated temperature can eliminate the flooding problem, it leads to the dehydration of the membrane and loss of membrane ionic conductivity. Therefore, many researchers pay attention to developing a new membrane that can be operated at temperatures above 100 °C and has a high conductivity at low humidity. In addition,