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Advances and challenges in alkaline anion exchange membrane fuel cells

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The last several decades have witnessed the rapid development of alkaline anion exchange membrane fuel cells (AAEMFCs) that possess a series of advantages as compared to acid proton exchange membrane fuel cells, such as the enhanced electrochemical kinetics of oxygen reduction reaction and the use of inexpensive non-platinum electrocatalysts, both of which are rendered by the alkaline medium. As an emerging power generation technology, the significant progress has been made in developing the alkaline anion exchange membrane fuel cells in recent years. This review article starts with a general description of the setup of AAEMFCs running on hydrogen and physical and chemical processes occurring in multi-layered porous structure. Then, the electrocatalytic materials and mechanisms for both hydrogen oxidation and oxygen reduction are introduced, including metal-based, metal oxide-based, and non-metal based electrocatalysts. In addition, the chemistries of alkaline anion exchange membranes (AAEMs), e.g. polymer backbone and function groups, are reviewed. The effects of pre-treatment, carbonate, and radiation on the performance of AAEMs are concluded as well. The effects of anode and cathode ionomers, structural designs, and water flooding on the performance of the single-cell are explained, and the durability and power output of a single-cell are summarized. Afterwards, two innovative system designs that are hybrid fuel cells and regenerative fuel cells are presented and mathematical modeling on mass transport phenomenon in AAEMFCs are highlighted. Finally, the challenges and perspectives for the future development of the AAEMFCs are discussed.

Contents

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1. Introduction

We have to adopt new energy supply technologies that utilize renewable energy sources [1–8], due to the current energy and environmental issues we are facing today. Among them, fuel cells have been considered as one of the most promising clean and efficient power generation technologies for a sustainable future [9–15]. Hence, tremendous efforts have been made on the development of fuel cells [16–22]. Alkaline fuel cells (AFCs) that use potassium hydroxide (KOH) solution as the liquid electrolyte have shown much success since the 1960s, particularly working as the energy supply devices powering the Gemini and Apollo spacecraft, due to the fact that the electrochemical kinetics of the oxygen reduction reaction (ORR) is much enhanced resulting from the alkaline environment, allowing the absence of expensive noble metals in preparing the electrocatalysts and thus reducing the cost of the fuel cell system [23–25]. Despite its compelling merits, however, this fuel cell technology has not made sufficient progress in market presence yet. One significant factor preventing widespread commercialization is the use of the alkaline liquid electrolyte, which may cause two problems [26]. One is the carbonate, the product of the side reaction between hydroxide ions in the liquid electrolyte and carbon dioxide in the air, reducing the concentration of hydroxide ions and potentially blocking the pores of the porous electrode via the precipitation of the metal carbonate [27–29]. The other is electrode flooding and drying problems, which are more likely to arise if the liquid electrolyte is not well controlled [30,31].

To address the issues caused by involving the liquid electrolyte, ion exchange membrane fuel cells that employ solid electrolyte have received ever-increasing attention [32–36]. The use of solid electrolyte membranes in fuel cells can remove the carbonate problem and avoid the liquid electrolyte management. Hence, extensive efforts have been devoted to developing alkaline AAEMFCs and remarkable achievements have been made [37–39]. In addition, many other advantages of the AAEMFCs are summarized as follows: (1) faster electrochemical kinetics of the ORR in alkaline media [40,41], (2) absence of noble metal electrocatalysts [42,43], (3) minimized corrosion problems in the alkaline environment [44,45], and (4) cogeneration of electricity and valuable chemicals [46–48]. Currently, compressed hydrogen and liquid alcohol are the most common fuels used in AAEMFCs. The liquid alcohols, e.g. methanol, ethanol, formate, and small polyalcohols, are convenient to handle, store, and transport [49–51]. Another advantage is that they are easy to be acquired from the abundant biomass, suggesting that the process is carbon-neutral and the sources are sufficient [52]. Borohydrides with high energy density are also recognized as a suitable fuel for AAEMFCs due to the fact that they are easy to handle, store, and transport as well. In addition, the products in the anode effluent can be converted back to borohydrides, which is beneficial for a sustainable future [18]. In consideration of degree of commercialization, this article will focus on the AAEMFCs running on hydrogen that is the maturest in commercialization. The objective of this review is to provide a general description of this type of fuel cell, introduce electrocatalytic materials for hydrogen oxidation and oxygen reduction reactions, summarize the alkaline anion exchange membranes (AAEM) and single-cell performance, as well as highlight the remaining challenges and future directions.

2. General description

In principle, the structure of AAEMFCs is just borrowed from proton exchange membrane fuel cells (PEMFCs), with the main difference that the solid membrane is an AAEM instead of a proton exchange membrane (PEM). In AAEMFCs, the charge carrier is OH^- transporting through the AAEM from the cathode to the anode, while H^+ works as charge carrier transporting through the PEM from the anode to the cathode in PEMFCs. Hence, AAEMFCs have been considered as an alternative to PEMFCs and garnered renewed attention recently due to the above-mentioned advantages. Currently, many researchers have put their focus on the synthesis of polymeric alkaline anion exchange membranes with high ionic conductivity and excellent chemical stability, as well as novel electrocatalysts that are favorable and low cost [53–63].

Like other fuel cells, a single AAEMFC consists of three main components, i.e. an anode, a cathode, and an AAEM, so-called membrane electrode assembly (MEA), as shown in Fig. 1. Specifically, the integrated multi-layered porous structure is constituted sequentially by an anode gas diffusion layer (GDL), an anode catalyst layer (CL), an AAEM, a cathode CL, and a cathode GDL. The GDLs in the anode and cathode that are both composed of two layers, a backing layer (BL) based on carbon paper or carbon cloth and a micro-porous layer (MPL) that is comprised of carbon powders mixed with hydrophobic polymer (typically PTFE). The CLs are usually made of electrocatalysts mixed with ionomer, resulting in the formation of triple-phase boundaries (TPBs) for the electrochemical reactions, i.e., hydrogen oxidation reaction (HOR) and ORR. Particularly, the GDL provides the support for the corresponding CL, distributes the reactants uniformly, and transports electrons to the current collector. Recently, Li et al. [64] proposed a metal foam-based electrode integrating the flow field, BL, MPL, and CL into a whole, which facilitates the mass