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Review article

Alkaline anion exchange membrane fuel cells for cogeneration of electricity and valuable chemicals

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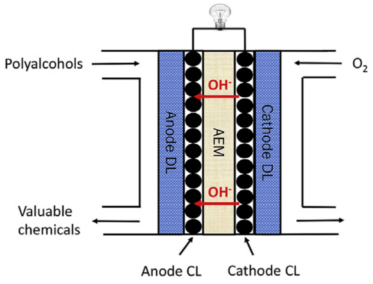
HIGHLIGHTS

- Fuel cells for cogeneration of electricity and valuable chemicals are reviewed.
- Various valuable chemicals and power output are summarized.
- Remaining challenges and future perspectives are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkaline anion exchange membrane fuel cells (AAEMFCs) have received ever-increasing attentions due to the enhanced electrochemical kinetics and the absence of precious metal electrocatalysts, and thus great progress has been made in recent years. The alkaline anion exchange membrane based direct alcohol fuel cells, one type of alkaline anion exchange membrane fuel cells utilizing liquid alcohols as fuel that can be obtained from renewable biomass feedstocks, is another attractive point due to its ability to provide electricity with cogeneration of valuable chemicals. Significant development has been made to improve the selectivity towards high added-value chemicals and power output in the past few years. This review article provides a general description of this emerging technology, including fuel-cell setup and potential reaction routes, summarizes the products, performance, and system designs, as well as introduces the application of this concept in the removal of heavy-metal ions from the industrial wastewater. In addition, the remaining challenges and perspectives are also highlighted.

1. Introduction

As the energy shortage issues and greenhouse gas effects are increasingly serious, fuel cells that are alternative options for power supply sources have attracted worldwide research interest due to its potential to alleviate the two challenges simultaneously [1–6].

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Fuel cells are one of the most promising clean and efficient energy production technologies that directly convert chemical energy stored in fuels to electricity and heat [7,8]. Generally, fuel cells can be classified into five types according to the electrolyte employed: alkaline fuel cells (AFCs), polymer electrolyte fuel cells (PEFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs) [9]. Among them, PEFCs and AFCs can be operated under ambient conditions, which allow their applications in our daily life, including electric vehicles and portable devices [10–13]. Furthermore, the replacement of liquid electrolyte by solid polymer electrolyte (i.e., ion exchange membrane) can overcome the problems of electrolyte leakage and carbonate precipitation [14–19]. The PEFCs can be divided into two types of fuel cell based on the employed membranes, i.e., anion exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFCs) [20,21]. Compared to PEMFCs, AAEMFCs have received ever-increasing attention recently, primarily due to the following advantages [22–24]: (1) faster electrochemical kinetics of the ORR in alkaline media, (2) the absence of noble metal electrocatalysts leading to the lower cost, and (3) the alleviated fuel crossover from the anode to cathode by the directional electro-osmotic drag from the cathode to anode.

Typically, as hydrogen and oxygen have been employed as fuel and oxidant in an AAEMFC, respectively, the final products are electricity, heat, and water. This case is the most representative in electricity generation without pollution emission. However, the issues associated with hydrogen production, transportation and storage overshadow the commercialization of H_2/O_2 fuel cells [25]. Hence, liquid alcohols derived from biomass that are renewable, cheap, and abundant are expected to be employed as fuels fed into the anode chamber [26,27]. To date, the complete electro-oxidation of alcohols including ethanol, ethylene glycol (EG), and glycerol to CO_2 has not been achieved under ambient conditions [28–30]. Although it remains a challenging task, the partial and selective electro-oxidation of polyalcohols provides a potential route to obtain valuable chemicals of industrial interest, such as tartronate, oxalate, and mesoxalate, etc. [31]. Particularly, mesoxalic acid that is 140 USD g^{-1} is the precursor to synthesize an anti-human immunodeficiency (HIV) agent [32]. In addition, mesoxalate is applied in the treatment of diabetes [33]. Tartronate acid whose price is as high as 1536 USD g^{-1} has been widely used in medicine industries [34], food industries [35–37], and anti-corrosive protective agents [38]. Hence, considerable researches have been conducted on simultaneous generation of electricity and valuable chemicals by using an AAEMFC and great progress has been made [39–43]. The objective of this review is to provide a general description of this type of device, summarize the various valuable chemicals and power output, introduce innovative system designs, as well as highlight the remaining challenges and future directions.

2. General description

In principle, the structure of AAEMFCs is just borrowed from 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. Generally, the critical component of a single AAEMFC is membrane electrode assembly (MEA) sandwiched between anode and cathode bipolar plates, which consists of an anode, an AAEM, and a cathode, as shown in Fig. 1. Specifically, the integrated multi-layered structure is composed of an anode diffusion layer (DL), an anode catalyst layer (CL), an AAEM, a cathode CL, and a cathode DL sequentially. Particularly, the DLs of the anode and cathode show the identical construction, both of which consist of a backing layer (BL) based on carbon paper or carbon cloth and a micro-porous layer (MPL) comprised of carbon powders mixed with hydrophobic polymer (typically PTFE). Additionally, the CLs are usually made of electrocatalysts mixed with ionomer, leading to the formation of triple-phase boundaries (TPBs) for electrochemical reactions. Typically, the functions of DL can be concluded as follows: (1) provide the support for the corresponding CL, (2) distribute the reactants uniformly, (3) realize the good water management, and (4) transport electrons to the current collector. The AAEM functions as a barrier to separate the anode and cathode, preventing the fuel crossover from the anode to cathode; meanwhile, it provides the pathway for conducting hydroxide ions. The released electrons by fuel electro-oxidation transport through the external circuit to complete the loop.

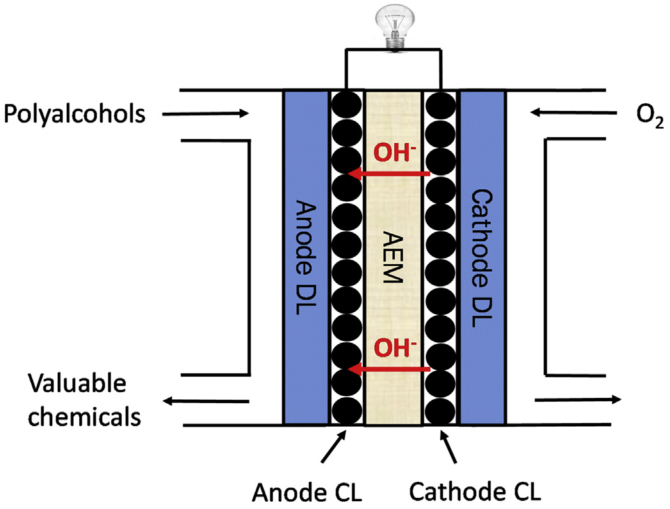

Fig. 1. Schematic of a typical alkaline anion exchange membrane fuel cell (AAEMFC).

It is worth mentioning that the fuel supply method is quite different from the conventional AAEMFC for power generation. Since the selective conversion ratio is the most critical parameter that is associated with the yield of the target product and the amount of the initial provided fuel, the supplied solution containing fuel and alkali should be cycled between the solution vessel and the anode chamber via a closed loop, usually employing a peristaltic pump, for a certain time.

As EG and glycerol that are derived from biomass are the two simplest polyols, herein the discussion of the reaction mechanisms is limited to EG and glycerol electro-oxidation. The reaction pathways of EG and glycerol electro-oxidation are illustrated in Fig. 2 (a). It is indicated that electro-oxidation of EG can go through two reaction routes, either the poisoning paths or the non-poisoning paths [44]. The final products of non-poisoning route are oxalate, glycolate, and glycoxalate, and it ends at oxalate due to its slow electro-oxidation on the existing electrocatalysts. Although oxalate is not the main product, it can be obtained by further electro-oxidation of glycolate or glycoxalate depending on pH. The final product of poisoning route is formate derived from the cleavage of C-C bond of glycolate. It should be noted that the applied potential plays an important role in C-C bond scission. When the potential is lower than 400 mV, no C-C bond cleavage occurs on Pt electrocatalyst, and the C-C bond of EG is cleaved at 500 mV, leading to CO poisoning [45]. It was reported by Demarconnay et al. [46] that the addition of Bi to Pt resulted in decreasing the onset potential of EG electrooxidation of about 70 mV and achieving higher current densities in the whole studied potential range. Furthermore, a