Renewable and Sustainable Energy Reviews 80 (2017) 669–678

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

From structures, packaging to application: A system-level review for micro direct methanol fuel cell

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ARTICLE INFO

Keywords:
µDMFC
Functional components
Packaging
Application

ABSTRACT

Micro Direct methanol fuel cell (µDMFC) has attracted wide attention in the field of portable electronic equipment because of its unique advantages such as no charge, environment friendliness, simple structure and convenient fuel storage. It has obtained important applications in laptop, mobile phones, micro-satellites, electric vehicles, MEMS devices, video camera and other aspects. So, it is significant to study in depth its structure, functional characteristics and applications. This review shows the progress on the recent development of micro direct methanol fuel cell. Lots of functional components including micro flow field plate, membrane electrode assembly, proton exchange membrane, catalytic layer, diffusion layer and collector are studied and discussed. The supplies management and packaging technology are also explained and discussed in detail. A mass of portable devices whose power are supplied by µDMFC are researched and discussed. This work will provide an comprehensive guide to those who want to study µDMFC.

1. Introduction

Fuel cell is a power generation device based on the electrochemical discharge. The current can be produced through electrochemical reaction of the fuel and oxidant. As a new type of clean energy, the advantages of fuel cells such as high energy conversion efficiency, high reliability, low pollution, low radiation, no noise, easy to start, environmentally friendly, etc., make it have a very broad application prospects in various types of portable electronic products [1,2].

Fuel cells are divided into five kinds of types including alkaline, proton exchange membrane, phosphoric acid, solid oxide and molten carbonate batteries. Due to the differences of the electrode, the electrolyte, and operating conditions, it makes different in the field of application. The most suitable for portable micro-systems, is the proton exchange membrane fuel cell (µPEMFC). This battery can work at room temperature, with small size, light weight, anti-aging, good life and so on. The direct methanol fuel cell in the proton exchange membrane fuel cell is fueled by liquid methanol solution, which saves fuel reforming and purification process. The fuel replenishment mechanism is very convenient, which makes the methanol fuel cell system more simple in structure design and has high security and reliability. As a fuel, Liquid methanol has many advantages including rich sources and low cost, and is its easy to carry and storage. It effectively solve the restricted problem of the hydrogen source existing in hydrogen-oxygen proton exchange membrane fuel cell, and is a very good renewable fuel. µDMFC has a greater advantage in portable equipment and has been widely concerned in academia and industry [3,4]. The first study of the DMFC model was carried out by the group represented by Scott at Newcastle University. They established a gaseous feed DMFC porous electrode model in one-dimensional state [5]. Then, according to the transfer of methanol in liquid feed DMFC, the concentration distribution and anodic polarization curve of methanol in the catalyst layer were obtained. The discharge curve of the battery was simulated by the empirical equation of open circuit voltage and cathodic polarization [6]. Kulikovsky et al. established a two-dimensional model of DMFC for gaseous feed and liquid feed, respectively. The concentration distribution and current distribution of methanol were investigated [7]. Wang et al. established a comprehensive DMFC two-phase flow model [8]. Baxter et al. combined with the microstructure of the anodic catalytic layer to establish a three-phase model of anodic catalytic layer consisting of catalyst, Nafion resin and pore [9]. Newman did a lot of work on the physical model of the electrolyte membrane and the establishment of the corresponding mathematical model [10–13]. In 2002, the German SFC (Smart fuel cell) company exhibited the first µDMFC product SFC A25 [14,15]. Toshiba Corporation developed the use of concentrated methanol feed µDMFC, The µDMFC can be directly connected to the laptop with the output power of 12 W, the use of 50CC of concentrated methanol (90%), and the laptop can work 5 h [16]. KIST (Korea Institute of Science and Technology) announced a µDMFC system for robot power

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http://dx.doi.org/10.1016/j.rser.2017.05.272
Received 23 May 2016; Received in revised form 7 May 2017; Accepted 29 May 2017
1364-0321/

supply. The system consists of 42 battery cells, and it work at 19.3 V when the output power of 400 W [17]. In addition, Japan's Sanyo, Panasonic, Electric (NEC), Fujitsu, LG and Sony, the US's Neah and MTI, South Korea's Samsung, China's BYD and many other companies have invested in the DMFC research and prototype display. Massachusetts Institute of Technology doubles the efficiency of μDMFC by changing the surface structure of the metal electrode [18]. Rashidi et al. found that μDMFC has advantages in terms of volume, weight and structure. Although the production cost is higher in short term use, the long-term cost of DMFC is lower than that of lithium battery [19]. Some important reviews have been provided by many scholars. Lu et al. reviewed the development of μDMFC for high power applications [20]. Nguyen et al. reviewed the progress of micromachined polymer electrolyte membrane of μDMFC [21]. Yao et al. described a high-power density, silicon-based micro-scale direct methanol fuel cell under development at Carnegie Mellon [22]. Neburchilov et al. described the polymer electrolyte membranes that were both under development and commercialized for direct methanol fuel cells [23]. Kamarudin et al. draw out the current challenges and development of μDMFC and also showed some marketing prediction in term of economics view [24]. Kundu et al. reviewed the different substrate materials used in micro-fuel cells for the suitability of the portable electronics [25]. Evans et al. reviewed microfabricated micro-solid oxide fuel cell membranes [26]. Sundarrajan et al. outlined the important parameters such as fuel, water, air and thermal managements to increase cell performance by material manipulation and design [27]. Li et al. reviewed the advances of direct methanol fuel cells from design, fabrication to testing with high concentration methanol solutions [28]. Kamarudin et al. addressed the challenges and the developments of and the applications of DMFC [29]. Leong et al. gave a comprehensive review for ion exchange membranes as separators in microbial fuel cells for bioenergy conversion [30]. Awang et al. reviewed the functionalization of polymeric materials as a high performance membrane for μDMFC [31]. Zamel provided an overview of the various works tailored to understand how each component in the catalyst's ink affects the stability and life-time of the layer [32]. Jahnke et al. provided a comprehensive overview of the state of the art in modeling of PEMFC, covering all relevant scales from atomistic up to system level as well as the coupling between these scales [33]. Sk et al. reviewed advances in porous nanostructured nickel oxides and their composite electrodes for high-performance supercapacitors [34].

So far, μDMFC has been used as power source for many portable devices such as laptop, mobile phones, micro-satellites, electric vehicles, MEMS devices, video camera and other aspects etc. However, some intractable issues, for example, design and fabrication of functional components, material selection, water management, heat management, cell assembly and packaging, still need to be solved. In this work, we aimed at providing a systematic and comprehensive guide for those who intend to study μDMFC. We review μDMFC mainly in some significant aspects including functional components, reagents management, packaging technology and application. The functional components are categorized into six subcategories as micro flow field plate, membrane electrode assembly, proton exchange membrane, catalytic layer, diffusion layer and collector. The supplies management and packaging technology are also explained and discussed in detail. a variety of portable devices whose power are supplied by μDMFC are researched and discussed. Finally, the focus goals of this paper are summarized.

2. Structure and operating principle of μDMFC

The μDMFC is comprised of flow field plate and membrane electrode assembly (MEA). The MEA is comprised of proton exchange membrane and the anode and cathode on both sides. The anode and cathode are composed of the diffusion layer and a catalytic layer with a porous structure, respectively. Fig. 1 shows the basic structure and operating principle of μDMFC with the aqueous solution of methanol as fuel.

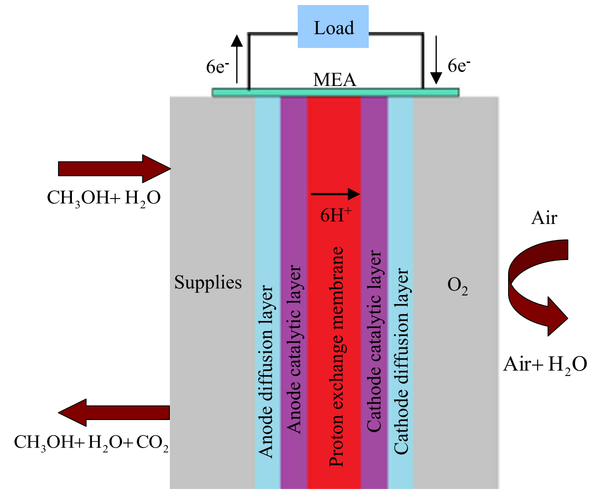

Fig. 1. The basic structure and operating principle of μDMFC.

While the μDMFC runs, the anode feed is methanol and water and the cathode feed is oxygen or air. Methanol and water can penetrate into the porous anode diffusion layer, and spread to the catalytic layer to occur the oxidation reaction to produce carbon dioxide, protons and electrons. Protons pushed by electric field migrate through the proton exchange membrane to the cathode catalyst layer. Electrons enter the cathode through an external circuit connecting the anode and cathode, and occur reduction reaction with oxygen penetrated into the cathode to produce water. μDMFC and external circuit form a loop to drive the load to work. The common electrode reaction in μDMFC is as follows:

at anode:

$$CH_3OH + H_2O \xrightarrow{Pt-Ru} CO_2 + 6H^+ + 6e^- \tag{1}$$

at cathode:

$$6H^+ + 6e^- + 3/2O_2 \xrightarrow{Pt} 3H_2O \tag{2}$$

The overall reaction:

$$CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2 \tag{3}$$

3. Functional components of μDMFC

3.1. Membrane electrode assembly (MEA) of μDMFC

MEA is a key functional unit that can generate electricity according to energy conversion. MEA consists of proton exchange membrane, the anode and cathode on both sides of the membrane. The anode and cathode consists of a catalytic reaction layer and a diffusion layer with porous structure, respectively. MEA is manufactured generally by using hot pressing membrane and electrodes together. For μDMFC, MEA needs to be made as thin as possible as limited by the size. A technical issue of MEA is the sealing problem from methanol leak. A lot of effective MEA fabricating technologies have been developed to prevent the methanol leak and improve the energy conversion rate of μDMFC.

Breitwieser et al. presented a fully spray-coated fuel cell membrane electrode assembly using aquivion ionomer with a graphene oxide/cerium oxide interlayer [35]. Pichonat et al. reported the fabrication of a new miniature fuel cell for portable applications based on a Nafion®-filled porous silicon membrane. This technique allows to combine advantages of Nafion® such as good proton conduction and silicon such as easy serial and parallel integration [36]. Xu et al. investigated experimentally a passive vapor-feed DMFC, which has a membrane vaporizer and a hydrophobic vapor transport layer, to improve its