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Polyoxymetalate liquid-catalyzed polyol fuel cell and the related photoelectrochemical reaction mechanism study

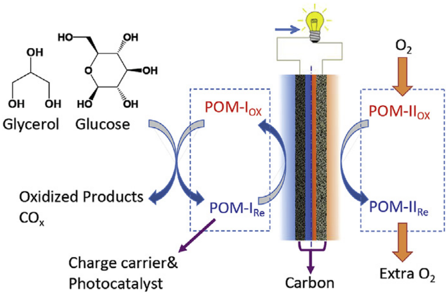
Weibing Wu [a, b, 1], Wei Liu [b, 1], Wei Mu [b], Yulin Deng [b, *]

[a] Jiangsu Co-Innovation Center for Efficient Processing and Utilization of Forest Resources, Jiangsu Provincial Key Lab of Pulp & Paper Science & Technology, Nanjing Forestry University, 159 Longpan Road, Nanjing 210037, China
[b] School of Chemical & Biomolecular Engineering and RBI at Georgia Tech, Georgia Institute of Technology, 500 10th Street N.W., Atlanta, GA 30332, USA

HIGHLIGHTS

- A polyoxometalate-catalyzed fuel cell favored by long-chain polyols is fabricated.
- The cell power density is dependent on the hydroxyl number of polyols.
- The photoelectrochemical reaction mechanism of polyol fuel cell is revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel design of liquid catalyzed fuel cell (LCFC), which uses polyoxometalates (POMs) as the photocatalyst and charge carrier has been reported previously. In this paper, the adaptability of biomass fuels (e.g., glycerol and glucose) to the LCFC and corresponding cell performance were studied in detail here. An interesting finding that greatly differs from conventional fuel cell is that high molecular weight fuels rather than small molecule fuels (e.g., methanol and ethylene glycol) are favored by the novel LCFC with respect to the power densities. The power output of LCFC strongly depends on the number and structure of hydroxyl groups in the biomass fuels. The evidence of UV–Vis and ^{1}H NMR spectra shows that the preassociation between POM and alcohol fuels, which determines the photoelectrochemical reaction pathway of POM, is enhanced as the number of hydroxyl increases. Experimental results also demonstrate that more hydroxyl groups in the molecules lead to faster photoelectrochemical reaction between POM and fuels, higher reduction degree of POM, and further higher power output of LCFC. Our study reveals that biomass-based polyhydroxyl compounds such as starch, hemicellulose and cellulose are potential high-performance fuels for LCFC.

1. Introduction

With increasing severity of worldwide fossil energy consumption and environmental problems, society faces the challenge to gain access to clean, reliable and renewable energy [1,2]. Currently, direct alcohol fuel cells (DAFCs) based on polymer electrolyte

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[*] Corresponding author.
E-mail address: yulin.deng@rbi.gatech.edu (Y. Deng).
[1] These authors contributed equally to this work.

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membranes are receiving increasing interest. Compared to combustion to produce thermal energy or conversion to biofuels via pretreatment, direct conversion of liquid alcohol fuel to clean electricity via DAFCs is a more prospective way. Methanol is one of the most common used fuel in DAFCs because it can be completely converted to CO_2 through electrical oxidation reactions on a Pt anode. However, methanol is toxic and volatile, which limits its application in low temperature direct fuel cells [3]. Many researchers have focused on using safer and more energetic higher alcohols (e.g., ethanol, ethylene glycol and glycerol) in DAFC applications [4,5]. However, higher alcohol fuels provide low energy conversion because of the low activity of noble metal to C—C bonds cleavage at low temperature [6–8]. In addition, the low power output of higher alcohol fuels and low resistivity of noble metal catalysts to the trace amounts of impurities are two other major challenges in DAFC development [3,9].

Using biomass-derived fuel in direct fuel cells is an attractive research area because of their non-toxic and abundant characteristics. However, biomass fuels, such as glycerol, glucose, starch, cellulose, and hemicellulose etc., have multiple carbons in their molecular chains. Therefore, biomass fuels cannot be effectively used in DAFCs with current fuel cell technology. The solid oxide fuel cell (SOFC) and microbial fuel cell (MFC) have been developed for biomass-to-electricity conversion using natural biomass-derived fuels [10–12]. However, SOFC usually requires high gasification temperatures of 500–1000 °C, and it is highly vulnerable to carbon buildup and sulfur-contaminants [13]. Although MFC can use enzyme or microorganism to decompose biomass at low temperature, their applications are still seriously hindered by formidable problems, such as high chemo-selectivity for substrates, rigorous reaction conditions, low electric power output and limited lifetime [14].

Recently, we reported a solar-induced hybrid fuel cell which realizes a new pathway for direct biomass-to-electricity conversion [15]. The distinguishing feature of the fuel cell is that polyoxometalates (POMs) function as a photo-catalyst and charge carrier to generate electricity. Soon afterwards, we further reported a completely noble-metal free and liquid-catalyst-mediated fuel cell (LCFC) with high performance improvement [16,17]. In LCFC, both fuel oxidation (anode) and oxygen reduction (cathode) are catalyzed in POM solutions, so both anode and cathode can be built as 3D electrodes and extended to several centimeters without technical limits. Unlike noble-metal catalysts, POMs are tolerant to most organic and inorganic contaminants. Therefore, raw biomasses, such as cellulose, starch, and even grass or wood powders can be used directly to produce electricity without prior purification. It is noteworthy that biomass fuels are more favorable than small molecule fuels (e.g., methanol, ethanol and formic acid) for the novel LCFC with respect to their power densities. It is an interesting finding that greatly different from conventional fuel cells, in which hydrogen and methanol are the best fuels. Most natural polymeric biomasses, such as cellulose, starch, hemicellulose and their oligosaccharide and monosaccharide, are polyhydroxyl compounds. Previous researches have pointed out that hydroxyl groups played an important role in the photoredox reaction of POM and alcohols [18–23]. However, no clear mechanism has been put forward. To deeply understand the effect of hydroxyl groups on the photoredox reaction of POM and the related performance of LCFC, a series of polyhydric alcohols with hydroxyl number from one to six were selected as fuels of LCFC. The main aim of this paper is to determine whether this type of LCFC is uniquely fit for biomass fuels. In addition, the performance of LCFC fueled by commercial glycerol and glucose was studied in details.

2. Experimental

2.1. Anode electrolyte solution via photocatalysis

Phosphomolybdic acid hydrate ($H_3[PMo_{12}O_{40}]$, PMo_{12}) was purchased from TCI America. Methanol, ethylene glycol, glycerol, erythritol, xylitol, sorbitol and glucose were purchased from Sigma-Aldrich. Calculated amount of phosphomolybdic acid and polyhydroxyl compounds were dissolved in DI water and then diluted to a certain volume. The starting pH of this solution was adjusted to 0.3 using concentrated phosphoric acid (85%, Alfa Aesar); thus, a clear yellow solution was obtained. The obtained yellow solution of PMo_{12} and fuel (15 mL) was kept at a constant temperature of 25 °C using a recirculating water bath (RM6 Lauda, Brinkmann Instruments Service Inc.). Next, the reaction solution was irradiated with a 250 W metal halide lamp (Bulbrite Industries E39 Mogul Base Enclosed Fixture) for required time with a distance of 15 cm from the solution surface. The color of the solution gradually changed from yellow to deep blue, and then the pH was adjusted to 3 with concentrated sodium hydroxide solution. During the light irradiation, a very small amount of solution was taken out as a sample and diluted to 1 mmol L^{-1} PMo_{12} for analysis of the concentration of reduced PMo_{12} using spectrophotometry method as discussed later. The obtained blue solution was directly used as the anode electrolyte in the fuel cell.

2.2. Preparation of cathode electrolyte solution

High-vanadium Mo—V-phosphoric heteropoly acid aqueous solutions with modified composition $H_{12}P_3Mo_{18}V_7O_{85}$ (noted as $P_3Mo_{18}V_7$) were synthesized according to the literature [24], using MoO_3 (Alfa Aesar), V_2O_5 (Alfa Aesar) and H_3PO_4 (Alfa Aesar). A typical synthesis process includes: 0.1575 mol (28.65 g) V_2O_5 was added to 1200 mL cooled DI water (~4 °C), then added with 180 mL H_2O_2 (Aldrich) with magnetic stirring and cooled by ice. After V_2O_5 was dissolved, 0.04 mol (4.6 g) of H_3PO_4 (85 wt%) was added and stirring at room temperature to decompose the extra H_2O_2 for 2 h. The obtained solution was noted as solution A. Then, 0.81 mol (116.64 g) MoO_3 and 0.095 mol (10.96 g) H_3PO_4 (85 wt%) were added into 1000 mL DI water, and heated to boiling. After the solution turned to yellow, 200 mL of the above solution A was gradually added (about 200 mL for one time) before the suspension was heated at its boiling temperature. After all the solution A was added, the suspension was boiled until MoO_3 dissolved completely and then evaporated to 150 mL. The concentration of $P_3Mo_{18}V_7$ solution obtained was 0.3 mol L^{-1}.

2.3. Assembly of direct biomass fuel cell and test methods

The direct biomass fuel cell was constructed using a Nafion 115 membrane sandwiched between two 3D graphite electrodes with no metal loading, as shown in Fig. 1. PMo_{12} and $P_3Mo_{18}V_7$ were used as anode and cathode catalysts, respectively. The bipolar plates of the fuel cell were made of high-density graphite plates with a serpentine flow channel 2 mm wide, 10 mm deep, and 5 cm long (total geometry projected area of the channel is 1 cm^2). The graphite felt was purchased from Alfa Aesar, and was pretreated with concentrated sulphuric and nitric acids in a 3:1 volumetric ratio at 50 °C for 30 min. Then the graphite felt was washed with DI water (until the pH of the wash water became neutral), dried at 80 °C and cut to pieces with 2 mm width and 10 mm thick. These graphite electrodes were filled into the channel of the bipolar plant. Nafion® 115 (127 μm thick, purchased from DuPonTM) was used as proton exchange membrane in this direct biomass fuel cell. The membrane was pretreated in the boiling solution of