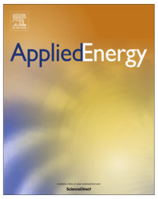
Applied Energy 200 (2017) 226–236

Contents lists available at ScienceDirect

Applied Energy

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



Innovative design of coal utilization – A green pathway for direct conversion of coal to electricity through flow fuel cell technology

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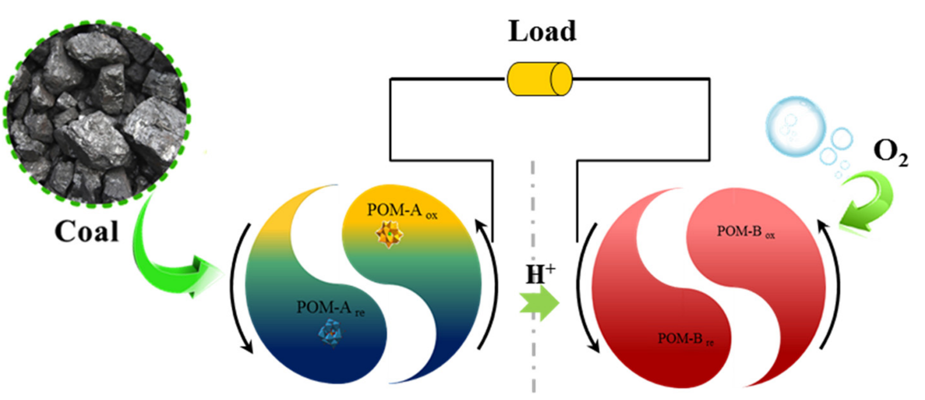
HIGHLIGHTS

- Direct conversion of coal to electricity at low-temperature was first achieved.
- Mechanisms are completely different from any reported coal fuel cells.
- Polyoxometalates were used as both catalysts and charge carriers.
- This process is low cost and environmentally friendly with high power density.
- Completely noble metal-free without complicated coal pretreatment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 January 2017
Received in revised form 24 March 2017
Accepted 6 May 2017

Keywords:
Fuel cells
Coal utilization
Green energy
Polyoxometalate
Chemical degradation

ABSTRACT

Low-rank coal, such as lignite, normally has low combustion heat and little commercial value. Combustion of low-rank coals will generate large amount of fly ashes and cause serious environmental problems. New technology for more effective use of low-rank coals with significantly less pollution is highly desired. In this study, we report an alternative method to convert coal chemical energy directly to electricity using flow fuel cell without complicated pretreatment. Practically, low-rank coal particles were first oxidized by polyoxometalate ($H_3[PMo_{12}O_{40}]$, denoted as POM-A) in solution on anode tank at 100–200 °C. The reduced POM transferred the accepted electrons to the anode of the flow fuel cell. These electrons passed through the external circuit and were captured by another polyoxometalate ($H_{12}[P_3Mo_{18}V_7O_{85}]$, denoted as POM-B) at cathode tank. The novel conversion method does not generate any fly ashes. The power density of the direct lignite flow fuel cell could reach as high as 120 mW cm^{-2}.

1. Introduction

Coal is the most abundant and economic fossil resources on the earth. The consumption of coal has increased from 4.92 billion to 7.43 billion tonnes from 2002 to 2012 [1]. Coal has been widely used as a solid fuel to produce electricity and heat by combustion through thermo power plants, from which more than 45% of electricity in the U.S. is generated [2]. However, the coal-fired power plants usually operate at low conversion efficiency (30–35%) and also produce serious air pollution problems [2]. Therefore, scientific attention has been focused on new technologies for coal utilization.

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http://dx.doi.org/10.1016/j.apenergy.2017.05.073
0306-2619/

Fuel cell devices can convert energy stored in chemical bonds into electricity directly and, thus, are regarded as a good alternative to coal-fired power plant due to its high energy conversion efficiency and little environmental effects [3]. However, the activation energy of electrochemical oxidization of carbon directly is high (109 kJ/mol) [4] and it only proceeds with a relatively high overpotential (over 1 V) at room temperature [5]. To address this issue, scientific researches were focused on the carbon fuel cell (CFC) [2,6–18], which use suitable chemical delivery vehicles for either carbon or oxygen in order to overcome the electrochemical oxidation barriers. Molten hydroxides [19,20] and molten carbonates [21–24] are usually used as electrolytes and oxygen vehicles in CFC. They increase the amount of electrochemical reaction sites by changing solid-to-solid interface between electrode and solid fuels into solid-to-liquid interface. However, in this kind of CFC arrangements, oxygen may be chemically incompatible with the electrolytes and have low solubility in it; besides, electrons' movement is also hindered in the molten electrolytes due to the poor conductivity. As a result, its performance and practical application are limited. Recently, solid oxide fuel cells (SOFC) have attracted tremendous attentions, in which a solid oxide electrolyte is always exploited to oxidize a gaseous fuel converted from coal particles [11,12,18]. The SOFCs are always accomplished with a coal gasification pre-treatment where oxygen [25], steam or dry CO_2 [26] are used and syngas is formed. Although the power density of SOFCs can reach over 100 mW/cm^2 [12], these arrangements can only operate at extremely high temperature [27] and is highly sensitive to poisonous impurities. Additionally, the energy cost of gasification process is high and the gas diffusion control process of a gaseous mixture is complicated, which cause the limitation of its large-scale application. Zecevic et al. [20] has argued that coal fuel cells operating at high temperature are non-practical and it is necessary to develop a practical coal fuel cell at low temperature with a good performance.

A half-cell of low temperature coal fuel cell using a secondary redox couple (Fe^{3+}/Fe^{2+}) to oxidize coal was reported by Douglas et al. [5]. However, they concluded that this approach was not practical because of the low reaction kinetics between redox pair and coal. Another attempt has been made by Teppei et al. [28], in which an aqueous-alkaline biocarbon fuel cell operates at ~250 °C. However, the performance was not promising and the apparatus was rather complicated. As far as we know, there is no technology that can convert coal into electricity directly at low temperature with high power output.

Polyoxometalates (POMs) are a class of anionic metal-oxo polyhedral clusters formed with metal centers and oxygen atoms at the vertices [29–31]. Due to the ability of undergoing highly reversible multi-electron redox reactions, POMs demonstrated great potential in the applications of energy storage, such as Li-ion batteries [32–35], sodium-ion batteries [31] and redox flow batteries [30,36]. A redox flow battery can store electrical energy in two redox couples [36,37], like (Fe^{2+}/Fe^{3+}, Cr^{2+}/Cr^{3+}) [38], (Zn/Zn^{2+}, Br_2/Br^-) [39] and (VO_2^+/VO^{2+}, V^{2+}/V^{3+}) [40–42]. Compared with these redox couples, POMs show their specific advantages due to their chemical and thermal stability. More importantly, most POMs can provide better capacities as highly multi-electrons transferring could be possible. Heng et al. [32] reported the reduction of 24-electrons in a discharging process when $TBA_3(PMo_{12}O_{40})$ was used. Based on these advantages, Harry et al. [30] reported a POM flow battery where ($SiV_3W_9O_{40}^{10-}/SiV_3W_9O_{40}^{13-}$) for application in stationary storage and found that the corresponding battery could be cycled 100 times with a coulombic efficiency over 95%. Besides, POMs have strong oxidative capability to degrade biomass by Wei et al. [43], which suggests its potential to decompose coal.

Technically, coal can be classified into different ranks according to the chemical structure and volatile content. Lignite, considered as the lowest-rank coal, has a relatively low heat content due to its low carbon content, high inherent moisture, and ash contents [44]. Generally, burning this type of low-rank coal in thermo power plants causes severe environmental issues mainly because of the contaminants and ash content. To increase energy-efficiency and to reduce pollution, environmentally-friendly conversion technologies are needed of great importance. Compared with the anthracite having dense polycyclic-aromatic-hydrocarbon structure, lignite is more likely to be degraded by POM ($H_3[PMo_{12}O_{40}]$) in solution on anode (POM-A) at 100–200 °C since its structure contains more reactive groups.

To the best of our knowledge, this is the first work that can generate electricity directly from traditional coal fuel with a high power output at low temperature. In this study, aqueous POM solutions, used as both catalysts and charge carrier [43], were applied to oxidize low rank coal and generate electricity directly through the proton-exchange membrane fuel cell system. In contrast to the current coal-fueled fuel cell technology, this direct coal flow fuel cell is completely different with a coal degradation temperature of 100–200 °C and a fuel cell operation temperature of 80 °C while the output power density is very promising, ~120 mW/cm^2. Potentially, the application of this innovative design for coal utilization may partially replace the current coal combustion power plants with a green and cleaner approach of great social and environmental significance. Besides, this fuel cell technology provides the possibility of changing the traditional coal-fueled centralized electricity generation to the distributed energy generation, which can be installed and applied in the household.

2. Methods

2.1. Preparation of anode electrolyte (POM-A)

Phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$) was purchased from TCI America. Phosphotungstic acid ($H_3[PW_{12}O_{40}]$) was purchased from Chem-impexInt'L INC (US). The addenda kegging type polyoxometalate $H_3[PW_{11}MoO_{40}]$ was synthesized by refluxing a solution of mixed phosphomolybdic acid and phosphotungstic acid with the mole ratio of 1:11 ($n(H_3[PMo_{12}O_{40}])$: $n(H_3[PW_{12}O_{40}]) = 1:11$) for 1 h. Then solution was concentrated by water evaporation at 80 °C to the concentration of 0.3 M.

$H_5[PMo_{10}V_2O_{40}]$ was synthesized according to the procedure as reported in literature [45,46]. In a typical synthesis, 24.4 g of sodium metavanadated was dissolved in 100 mL of DI water. The mixture was then heated to boiling temperature. Afterwards, 7.1 g of Na_2HPO_4 in 100 mL of water was mixed. 5 mL of H_2SO_4 (98%) was added dropwise after the solution was cooled down and, in the meanwhile, its colour changed to red. 121 g of $Na_2MoO_4 \cdot H_2O$ was dissolved in 200 mL of DI water and then mixed with the pre-prepared red solution. 85 mL of H_2SO_4 (98%) was added dropwise into the mixture under vigorous stirring and finally, a homogeneous solution formed. 500 mL of ethyl ether was used to extract $H_5[PMo_{10}V_2O_{40}]$ molecules. After evaporating all the ether, the solid part was dissolved in DI water, concentrated, and crystallized.

2.2. Preparation of cathode electrolyte (POM-B)

$H_{12}[P_3Mo_{18}V_7O_{85}]$ solution was used as cathode electrolyte and was synthesized according to Odyakov's work [47]. A typical synthesis process includes: (1) Preparation of solution A: 25.48 g