



Contents lists available at ScienceDirect

Applied Energy

journal homepage: [www.elsevier.com/locate/apenergy](http://www.elsevier.com/locate/apenergy)

# A microreactor with superhydrophobic Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coating concerning oxidation of hydrogen off-gas from fuel cell

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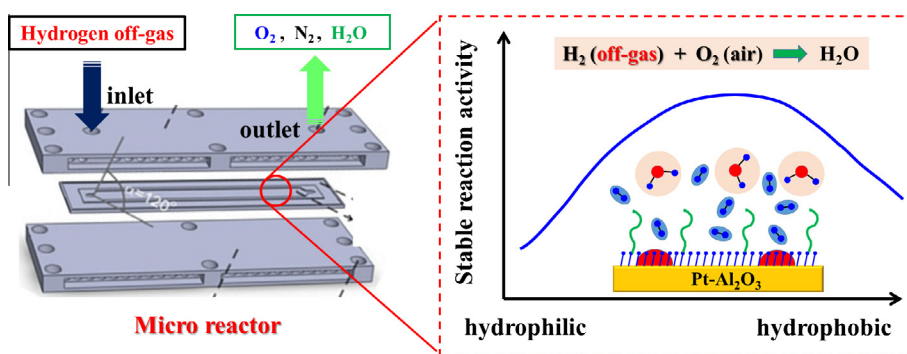
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## HIGHLIGHTS

- Pt–Al<sub>2</sub>O<sub>3</sub> was modified to superhydrophobicity via grafting by FAS.
- Hydrophobic modification greatly promoted catalytic activity and stability.
- Catalytic activity heavily depended on hydrophobicity extent in humid condition.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 7 September 2015  
Received in revised form 13 January 2016  
Accepted 19 January 2016  
Available online xxx

### Keywords:

Microreactor  
Hydrogen oxidation  
Fuel cell  
Hydrophobic  
Catalyst coating

## ABSTRACT

For polymer electrolyte fuel cells (PEFCs), Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coatings were developed to convert hydrogen off-gas of PEFCs to water. To ignite the hydrogen oxidation at room temperature with negligible induction period, the Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coatings on the walls were modified from hydrophilicity to superhydrophobicity via grafting by 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FAS). The modified Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coatings were optimized in a channel plate reactor (CPR) that is similar to microchannel reactors in flow pattern, but is much simpler to be fabricated and can be used repeatedly. We showed that higher grafting density of FAS provided stronger repulsive force on produced water vapor (favorable effect) while more resistance for the reactants approaching to catalytic active sites (unfavorable effect). The suitable hydrophobic modification significantly promoted the catalytic activities and stabilities of the catalyst coatings under both humid and dry feed stream conditions. Under the humid feed stream condition, the most active catalyst coating of 5WM–Pt–Al<sub>2</sub>O<sub>3</sub> showed the biggest contact angle of 150° and decreased the hydrogen concentration from 4 vol% to 632 ppm without a detectable induction period at 303 K. The microchannel reactor with superhydrophobic catalyst coatings showed great potential for conversion of hydrogen off-gas of PEFCs to water.

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## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been extensively used due to their high efficiency, low emission and friendliness to environment [1–5]. In most PEFCs, hydrogen is recirculated back

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into the feed stream (dead-end anode PEFC), thereby increasing the system efficiency [6–9]. Nitrogen and water from the air, which permeate from the cathode to anode through the membrane, get concentrated in the anode due to recirculation [8]. The PEFC stack rated performance in terms of output DC current and voltage can be significantly diminished by build-up of nitrogen and water which would reduce the concentration of hydrogen in the anode [10,11]. Also the electrodes flooding by water at the anode obstructs hydrogen molecules to reach cell reaction sites effectively. To remove excess water and impurities inside the PEFC, it is necessary to operate a periodic purging [12–15]. During purging, in addition to impurities, excess water and inert gas, also a quantity of hydrogen is discharged and thus it is not used by the PEFC electrochemical reactions. When fuel cells are used in the enclosed spaces and the semienclosed spaces such as deep tunnels, or in environments such as spacecraft [16] or underwater craft [17,18] where exhaust is hindered, the discharged hydrogen should be treated for safety reasons [19–22]. In addition, several reports claimed that the discharged hydrogen has an influence on the chemical composition of atmosphere [23–29]. The major tropospheric trace gas (mean concentration of hydrogen in the troposphere is about 520 ppbv [25]) has an effect on the levels of the hydroxyl radical (OH) and hence increases the lifetime and forcing of methane. Large-scale emission of hydrogen could enhance the climate change. If a global hydrogen economy replaced the current fossil fuel-based energy system and exhibited a leakage rate of 10%, it would produce a climate impact of 6% of the current fossil fuel based system [24].

To handle the discharged hydrogen safely and minimize the resulting environmental impact, catalytic oxidation has been proposed. Compared with conventional fixed-bed reactors, micro-channel reactors with catalyst coatings show negligible external and internal mass transport limitations as well as enhanced heat transport characteristics [30–35]. Consequently, these reactors have advantages, such as rapid heating and cooling, suppression of hot spots, fast response rates, and easy integration with miniaturized devices. Recently, catalytic micro combustors have been developed by several investigators, whose hydraulic diameter is smaller than the quenching distance of hydrogen combustion [36]. For a low Pt loading, as reported by Janicke et al. [37], the initial reaction temperature should be kept above 353 K in order to ignite the hydrogen oxidation, and this required an electricity heater. For a high Pt loading, the hydrogen oxidation could be ignited at room temperature with an induction period over 90 min to obtain a high hydrogen conversion. However, this long induction time is difficult to be achieved considering the discharge hydrogen off-gas of PEFCs is periodic. Moreover, the discharged hydrogen contains water vapor [38,39] which may further prolong the induction time. Therefore, it is desirable to develop a microreactor for hydrogen off-gas conversion operated at room temperature with negligible induction time.

The product of hydrogen oxidation is water ( $H_2 + 1/2 O_2 = H_2O$ ), and for the Pt based catalysts, it is known that the produced water vapor influences the activity of supported Pt catalysts in three ways. First, water molecules compete with the reactant molecules from being adsorbed on the surface Pt sites, and hereby affecting the adsorption and thereafter the activation of hydrogen and oxygen. Not surprisingly, this finally leads to a decrease in Pt catalytic activity. Second, the accumulation of water on the support through the mechanisms of adsorption and capillary condensation can affect the interaction between Pt and support, deactivating some surface active sites [40]. Third, it has been reported that the mass transfer resistance in wetted pores was remarkably higher than that of air-filled pores [41,42]. To minimize these detrimental effects of water, catalysts featuring hydrophobic supports have been extensively attempted. For instance, Zhang et al. prepared a

Pt/fluorinated carbon/ceramic (Pt/FCC) displaying significantly higher activity than the Pt/alumina catalysts because the hydrophobic FCC hinders the adsorption of water onto the support [40]. Jeffrey [43] prepared a 0.3 wt% Pt/activated carbon catalysts for the oxidizations of benzene, toluene and xylene (BTX) below 200 °C with BTX concentration ranging from 640 to 2000 ppm in air. Moisture reduced the activity slightly compared to Pt/ $Al_2O_3$  due to the hydrophobicity of the activated carbon. Hu et al. prepared two kinds of hydrophobic catalysts for the separation of hydrogen isotopes from liquid water in heavy-water reactors [44]. Carbon-supported  $Pt_3Fe$ -MI-H catalyst prepared by a modified microwave-irradiated ethyl glycol reduction procedure showed the highest activity under the same experimental conditions. Nevertheless, because of their inflammability and difficulty in coating the walls of the microreactors, those carbon based hydrophobic supports are inapplicable to microreactors in terms of hydrogen oxidation. Iwai et al developed an inorganic hydrophobic Pt catalyst named H1P for room-temperature oxidation of hydrogen isotopes released in a nuclear facility [45]. The overall reaction rate constant of the H1P catalyst was considerably larger than that for the traditional Pt- $Al_2O_3$  catalyst. The reaction rate for H1P in the presence of saturated water vapors lightly decreased compared with the reaction rate in the absence of water vapor owing to the excellent hydrophobic performance of H1P. Hydrophobic supports for catalytic hydrogenation of methyl acrylate were reported by Omota et al. [46]. Hydrogen consumption of hydrophobic Pd-SiO<sub>2</sub> is six times higher than hydrophilic Pd-SiO<sub>2</sub> catalyst at 293.7 K under reaction pressure of 104.1 kPa. Despite great success achieved on the hydrophobic catalysts, to our best knowledge, no progress on the hydrophobic catalyst coating for microreactor concerning hydrogen oxidation has been reported.

Most ceramic materials are made from metal oxides such as alumina, zirconia and silica. Whereas these materials are hydrophilic in nature owing to the presence of hydroxyl groups on their surfaces [47], they could be modified into hydrophobic ones by using different methods [48,49]. Fang et al. developed hydrophobic porous alumina ceramic hollow fiber membranes via grafting with fluoroalkylsilane (FAS) for water desalination based on a membrane distillation process [50]. It is interesting to prepare a hydrophobic Pt- $Al_2O_3$  catalyst coating by surface modification for the microreactors concerning hydrogen oxidation. However, there are few reports on the catalyst hydrophobic surface modification.

In this study, a catalytic microchannel reactor (hydraulic diameter is smaller than the quenching distance of hydrogen combustion) concerning hydrogen oxidation was developed. During the catalyst coating optimization, a channel plate reactor (CPR) was used instead due to its simplicity on fabrication and repeated usage. The catalyst coating Pt- $Al_2O_3$  was treated by hydrophobic modifications via grafting with FAS (1H,1H,2H,2H-perfluorooctyl triethoxysilane, Aladdin). The catalyst coatings were characterized by a number of characterization methods, including transmission electron microscopy (TEM), scanning electron microscope (SEM), contact angle measurement, Fourier transform infrared spectroscopy (FTIR) and X-ray photoemission spectroscopy (XPS). The effects of different hydrophobic modifications on the reaction efficiency were investigated by experiments combining with dissipative particle dynamics (DPD) simulations.

## 2. Experimental

### 2.1. Catalyst preparation

Fig. 1(a) shows the individual components of the CPR [30]. A top cover sheet with two holes was used as the inlet and outlet. The active catalyst coating was placed on the upper and lower walls

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