

Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

The influence of ethene impurities in the gas feed of a PEM fuel cell

Katrin Kortsdottir*, Rakel Wreland Lindström, Göran Lindbergh

Applied Electrochemistry, KTH – Royal Institute of Technology, Teknikringen 42, 10044 Stockholm, Sweden

ARTICLE INFO

Article history:

Received 19 March 2012

Received in revised form

21 June 2012

Accepted 29 June 2012

Available online 10 October 2012

Keywords:

PEM fuel cell

Impurity

Ethene

Pt/C

Stripping voltammetry

Mass spectrometry

ABSTRACT

Hydrogen produced by reforming may contain traces of hydrocarbon contaminants. These traces may affect the performance and lifetime of a fuel cell run on reformat-hydrogen. This study treats the influence of low concentrations of ethene on the adsorption and deactivation chemistry in a polymer electrolyte membrane (PEM) fuel cell. The study employs mainly cyclic voltammetry accompanied with an on-line mass spectrometer to analyse the outlet gas. Results from adsorption and desorption, by either oxidation or reduction, are presented, and the influence of adsorption potential, temperature and humidity and the presence of hydrogen are discussed. The results show that the adsorption of traces of ethene in a fuel cell is highly dependent on adsorption potential and that ethene adsorbs on Pt catalyst in a limited potential window only. Ethene cannot displace adsorbed H and is oxidised already at potentials of 0.6 V versus RHE at 80 °C, where the only detectable product is CO₂. A considerable part of ethene adsorbed at potentials above the hydrogen adsorption/desorption region can be reduced at low potentials and is desorbed as methane or ethene. Overall, the effect of low concentrations of ethene in the hydrogen feed on fuel cell performance is minimal, and no significant loss in cell voltage is found when ethene contaminated hydrogen is fed to a fuel cell running on hydrogen and oxygen at a constant load at 80 °C and at highly humidified conditions.

Copyright © 2012, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The proton exchange membrane (PEM) fuel cell technique is very promising for electricity production for automotive, stationary and mobile applications, mainly for its high efficiency and low emissions. Despite its many advantages there is a major drawback; the heart of the fuel cell, the membrane electrode assembly (MEA), is sensitive to contaminants.

The purity of the hydrogen gas is strongly dependent on the source of the hydrogen. While hydrogen produced by electrolysis is essentially clean, hydrogen rich gas produced by reforming of fossil- or bio-fuels contains considerable

amounts of carbon monoxide (CO), carbon dioxide (CO₂), and nitrogen. In addition, small amounts of organic impurities (ppm levels) and sulphur-containing species may be present. Some of the gaseous species, such as CO and those containing sulphur, are known to be highly poisonous for the MEA and must be removed from the gas flow before it enters the fuel cell. Sulphur species are normally trapped in a sulphur sink, and CO is transformed into the less harmful CO₂ by reverse water gas shift reactions or preferential oxidation. The reverse water gas shift has the advantage that hydrogen is produced in the process and is often followed by a preferential oxidation step to optimise the removal.

* Corresponding author. Tel.: +46 8 790 6506.

E-mail address: kiko@kth.se (K. Kortsdottir).

Although an increased interest for impurities in fuel cells has arisen in the last decade [1–4], the effect of organic impurities has not been much studied. In order to optimise the cleaning steps for reformat-hydrogen, it is important to investigate the effects of these impurities. We have previously studied the effect of toluene, chosen as a representative for aromatic compounds, as an impurity in hydrogen gas [5]. That study indicated that even though concentrations of about 100 ppm of toluene caused no immediate problems to the performance of the fuel cell, prolonged exposure times resulted in a reordering of the adsorbed layer into a more strongly bound species. Higher concentrations of toluene were found to hamper the kinetics of hydrogen adsorption, thus confirming that hydrocarbon impurities in the hydrogen feed can cause problems for the fuel cell performance.

Ethene is the smallest alkene and as such it is a good model compound for alkenes in general. Also, it is produced industrially in huge quantities, e.g. for polyethylene plastic production, and is known to form in reformers, although the quantity may differ considerably depending on the design of the reformer [6,7]. Ethene has also been shown to be present in the exhaust gas of vehicles engines [8,9], and consequently, it is present in the atmosphere in a few tens of ppb [8,10]. Thus, ethene may be present both at the anode and the cathode in a fuel cell.

The interaction of ethene and platinum has been extensively investigated in the past, in vacuum, under gaseous conditions and in solution, electrochemically and non-electrochemically and has also been tested as a direct fuel for fuel cell in the 1960s [11–17]. The adsorption of ethene from gaseous phase [18–25] differs considerably from that of a liquid phase [20,21,24,26–30], while in both cases temperature, crystal structure and adsorption potential, where applicable, affect the adsorption process. At temperatures below $-73\text{ }^{\circ}\text{C}$, gaseous ethene adsorbs on Pt in vacuum as π - or di- σ -bound ethene, while at around $-33\text{ }^{\circ}\text{C}$, dehydrogenation of the adspecies begins a transformation to ethylidyne ($\equiv\text{CCH}_3$). This irreversible transformation is not yet complete at room temperature [18,20–23,25]. In vacuum at room temperature, the main adsorption species of ethene on Pt has been shown to be ethylidyne, a species that has also been shown to form when ethene is allowed to adsorb on Pt at atmospheric pressure at room temperature, although to less extent [24]. In studies on the adsorption of ethene on Pt in aqueous electrolyte three chemically different adspecies were originally identified [26]: a hydrogenatively desorbable species, a cathodically non-desorbable species and an oxygen-containing species. The hydrogenatively desorbable adspecies was later shown to be two different adspecies with slightly different chemical properties, where one binds more weakly to Pt than the other and can be displaced by I^+ , Cu^{2+} or CO [20,21,27,29]. The displaceable adspecies has been suggested to be π -bound ethene and is displaced as ethene [21,29], while the more strongly adsorbed species is suggested to be di- σ -bound ethene [30]. Both these species, π - and di- σ -bound ethene, are hydrogenatively desorbable as ethane and butane at low potentials. The cathodically non-desorbable species, but non-oxygen containing, is bound much more strongly than the previous two described, and is the predominating species formed on Pt(111). It can only be desorbed by oxidation at

potentials above 1.0 V [26,27], even at elevated temperatures [20]. This cathodically non-desorbable species has been suggested to be ethylidyne [21,26], which according to Wieckowski et al. [24] is too stable to be a hydrogenation intermediate at room temperature. Finally, the oxygen-containing species is mainly formed at higher potentials, and in larger amounts on Pt(110) and polycrystalline Pt than on Pt(111) [26–28]. Baltruschat and co-workers [20,21,26–28,30] suggested that this oxygen-containing species, which is formed via partial hydration during adsorption has the form of C–C–O, i.e. that the C–C bond is not cleaved during adsorption. The adsorbate decomposes to methane and adsorbed CO at low potentials. The formation of adsorbed CO during the reduction of ethene has been confirmed by FTIRS [31,32]. Not all studies agree on the existence of this C–C–O adsorbate. Gootzen et al. [31] have suggested such an adspecies would be unstable and would dissociate even at high coverages and Berna et al. [33] claim adsorbed CO to be the only adspecies that contains oxygen.

Although these studies in liquid electrolyte may give some indication of how impurities may affect the operation of a fuel cell, their results cannot be directly transferred to a real fuel cell environment. The conditions in a fuel cell are very different from those in liquid electrolyte. Most important is the co-existence with hydrogen gas, but also that the system is humidified and generally operates at elevated temperatures. Further, although the ion conductive media in the solid electrolyte is based on water, the narrow channel system through the polymer is much different from bulk water, and, in principle, only protons and small cations are conducted.

This study is a continuation of our previous study on toluene as a representative of aromatic hydrocarbons [5], where ethene serves as a representative of unsaturated hydrocarbons as impurities in the anode gas flow of a PEM fuel cell.

2. Experimental

2.1. Preparation of membrane electrode assemblies (MEAs)

The membrane used in the study was Nafion 115, purchased from DuPont. The membrane was cleaned by boiling in a 3% $\text{H}_2\text{O}_2(\text{aq})$ solution for 1 h, followed by a quick rinse in milli-Q water before boiling in 0.5 M H_2SO_4 for another hour. To conclude the cleaning process, three consecutive milli-Q water baths were brought to the boil for a few minutes.

The electrode ink was prepared by mixing the catalyst powder and Nafion ionomer solution using milli-Q water and isopropanol in equal volumetric amounts as solvent. The catalyst used in the study was 36% Pt on high surface carbon (TEC10E40E from Tanaka) with a mean Pt particle size of 3 nm and the ionomer solution was 5 wt% Nafion from DuPont.

The ink was ultrasonicated and stirred over-night before being applied with a pipette on the membrane, which was placed on a heated table at $90\text{ }^{\circ}\text{C}$ to aid the evaporation of solvent. The membrane was pressed flat at $130\text{ }^{\circ}\text{C}$ just before applying the ink to simplify the procedure. The resulting electrode had a loading of approximately 0.1 mg Pt and an area of approximately 0.5 cm^2 . The Nafion content in the dry

Download English Version:

<https://daneshyari.com/en/article/1274398>

Download Persian Version:

<https://daneshyari.com/article/1274398>

[Daneshyari.com](https://daneshyari.com)