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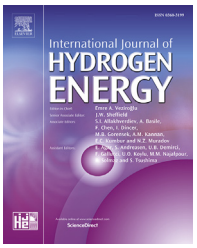

Influence of ethyl acetate as a contaminant in methanol on performance of Electrochemical Methanol reformer for hydrogen production

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ABSTRACT

Organic solvents like methanol is commonly used in pharmaceutical industries as a separation media in the purification process of drugs, and it contains various contaminants like ethyl acetate, methyl formate, acetic acid, etc. in the effluent stream. In the aspect of utilizing this industrial waste/effluent, we attempted to generate pure hydrogen by Proton Exchange Membrane (PEM) based Electrochemical Methanol Reformation (ECMR) process. The present study reports, the influence of ethyl acetate as a potential impurity in methanol on performance of ECMR cell for hydrogen production. Initially, electrochemical half-cell studies carried out using various concentrations of ethyl acetate (0.25, 0.5 and 1%) and their effect was studied systematically. In addition, the ECMR full cell performance was also evaluated with these concentrations and performance deterioration observed during long operation hours and discussed the possible regeneration method in view of its further practical development. The observed cell performance deterioration was attributed to formation of reaction intermediates during oxidation of methanol-water, which was identified by using FTIR and NMR analysis. Potentiostatic mode with operating potential of ~0.86 V was used as a method to regenerate the cell performance.

Introduction

Hydrogen can be considered as a clean energy carrier because when it is used (either in fuel cells or IC engines), the only by-product generated is water. It is essential to produce hydrogen efficiently in a cost-effective manner for creating society with Hydrogen energy. Hydrogen global production has so far been dominated by fossil resources like coal, biomass and other renewable sources and also with the most significant technologies like steam reforming of hydrocarbons [1–3] but their amount is limited and will be exhausted in few decades. The state-of-the-art onsite hydrogen generators now in use are based on electrolysis of water [4–6], which requires more energy to produce hydrogen gas. Electrochemical methanol reforming (ECMR) using methanol water mixture is one of the

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best ways to generate hydrogen with lower power consumption than a water electrolyzer [7–11] by applying an electrical potential across two electrodes separated by a proton exchange membrane (PEM). This process leads to economic way for hydrogen generation even when the cost of methanol is considered. Methanol is readily available electroactive alcohol, which can be economically produced from non-renewable sources such as natural gas, coal and renewable sources such as biomass and has high energy density similar to gasoline [12–15]. In India, demand for methanol has been growing steadily at 7.1% per annum since 2010, and it has been driven by pharmaceuticals and formaldehyde industries. Methanol is being primarily used as a separation media during drug purification stages in the pharma industry and has various potential impurities such as ethyl acetate, chloroform, etc in the effluent stream. The objective of this work is to use the industry effluent rich in methanol from these industries for reforming to generate pure hydrogen. In the present work, an attempt has been made to investigate the influence of one of the impurities of ethyl acetate on methanol oxidation in ECMR for pure hydrogen production by doping various concentration of ethyl acetate in methanol-water mixture. The effect of operating parameters like applied potential, concentration of contaminants and durability of the cell were systematically studied. In addition, the performance deterioration of the cell during longer operation has been studied in conjunction with its further regeneration given its possible practical application. To the best of our knowledge hydrogen production through ECMR using such contaminated reactant studies on methods of continuous operation, its performance deterioration, and recovery and product analysis have not been carried out in detail. The study is further important as an attempt has been made to explore the effect of contaminant that contains four carbon atoms which are difficult to oxidise is used.

Experimental

Electrochemical studies

Initially, the influence of ethyl acetate as a contaminant on methanol oxidation has been investigated using cyclic voltammetry and potentiostatic techniques by Solartron analytical cell test system 1400 in conventional three electrode cell setup. As the reactant, we prepared 0.5 M H_2SO_4in 2 M methanol solutions containing various 0.25, 0.5 and 1.0 wt% of ethyl acetate as a contaminant. Carbon supported 40% Pt 20% Ru electrocatalyst slurry was coated on glassy carbon electrode which was used as working electrode, saturated calomel electrode as the reference electrode and Pt counter electrode was used.

Fabrication and evaluation of ECMR cell

The performance of ECMR was carried out using conventional electrolyser set up which includes end plates, current collectors, heating coils, straight parallel flow field machined graphite plates and membrane electrode assembly (MEA). MEA of active electrode area 30 cm^2 was fabricated using Nafion® 117 membrane and carbon supported PtRu electrocatalyst (40% Pt 20% Ru on C), and carbon supported platinum (20% Pt on C) electrocatalyst was used as anode and cathode with loadings of 3.0 mg/cm^2 and 0.5 mg/cm^2respectively. The catalyst suspension was made by mixing respective catalyst in isopropyl alcohol and five wt.% Nafion solution and was coated on gas diffusion layer (GDL) coated carbon substrate from M/s. Ballard Power Products, USA. The prepared catalyst coated GDL placed on both sides of the membrane and hot pressed at 130 °C at 35 kg cm^{-2} for 3 min. The fabricated MEA was placed in between two graphite flow field plates and were clamped together with end plates using nuts and bolts, by applying uniform torque, to develop the electrolyser cell.

The electrolysis was conducted by circulating pure 2 M methanol and ethyl acetate contaminated methanol at anode compartment using a peristaltic pump and applying the voltage across the two terminals using programmable DC power supply (Model 62012P–40–120, M/s. Chroma ATE Inc, Taiwan). The potential and current polarisation of the cell was recorded at various operating temperature while operating with both pure methanol and ethyl acetate contaminated methanol. Life test measurement was made to examine the influence of ethyl acetate by operating electrolysis at constant current at 60 °C with and without ethyl acetate. To understand the mechanism of methanol oxidation, the samples before and after electrolysis were collected and FTIR and H^1- Nuclear Magnetic Resonance analysis using BRUKER instruments were employed to characterize the oxidised products of methanol and ethyl acetate contaminated methanol.

Results and discussion

Cyclic voltammetry studies

The influence of ethyl acetate addition in methanol oxidation reaction on carbon supported PtRu electrocatalyst was studied using cyclic voltammetry study in 0.5 M H_2SO_4+ 2 M CH_3OH Solution at the scan rate of 20 mV/s.The methanol oxidation peak in Fig. 1 was observed at 0.55 V with 0.131 A/cm^2 current density. The decrease in methanol oxidation peak current was observed while 0.5 wt % ethyl acetate was added with the positive shift in methanol oxidation peak potential. It may be attributed to the poisoning effect of ethyl acetate or the intermediates formed during oxidation that is strongly chemisorbed to the catalyst surface.

To investigate the observed decrease in methanol oxidation peak current, the experiments were carried out by holding the working electrode potential above the methanol oxidation peak potential observed in the presence of ethyl acetate (i.e.0.86 V) at different duration. Application of higher potential causes the activation of water molecules to produce OH species, which led to the oxidation of adsorbed intermediates [16]. Fig. 1 it also shows the CV curves obtained for methanol oxidation reaction after performing the potentiostatic test at different duration. It is observed that, peak current increases and peak potential shifts towards less positive direction with increasing duration of potentiostatic experiments. It indicates the decrease in methanol oxidation current was mostly due to the poisoning of electrocatalyst either by

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