

Electrochemical impedance spectroscopy study of methanol oxidation on nanoparticulate PtRu direct methanol fuel cell anodes: Kinetics and performance evaluation

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Abstract

Electrochemical impedance spectroscopy (EIS) along with cyclic voltammetry (CV) has been applied as a tool for the mechanistic investigation of methanol oxidation on nanoparticulate PtRu fuel cell anodes of a commercially available state of the art membrane electrode assembly (MEA). The spectra could be fitted to a circuit derived analytically for multi-step single adsorbed intermediate reactions. The analysis has indicated that methanol adsorption and surface blocking occur below the onset and the surface is 'poisoned' to the highest degree just before the onset, implying that the removal of residues before the onset, if any, is slower compared to the formation. The onset potential is marked by a sudden change in the mechanism as the impedance becomes pseudoinductive. It has also been demonstrated that EIS can be applied for analyzing and singling out different contributions behind electrode performance for methanol oxidation reaction under fuel cell operating condition.

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1. Introduction

Depletion of petroleum reserves, global warming and the concern about energy security have inspired the search for new energy carriers other than petroleum. Methanol is an excellent energy carrier because it is liquid at room temperature and pressure and can be produced from diverse sources including natural gas, coal and biomass. The fact that methanol is liquid makes it especially attractive as an energy carrier in mobile applications. Unlike hydrogen, storage of methanol is not problematic and if methanol is used as fuel, the existing fuel infrastructure could be utilized without much modification. Although, using methanol as fuel in road transportation will not eliminate the emission of CO₂ to the atmosphere, the inherent higher efficiency of fuel cells compared to internal combustion engines could substantially lower the emission of CO₂ [1]. In direct methanol fuel cells (DMFC), methanol can be fed directly for

the purpose of converting chemical energy to electrical energy. Besides transportation applications, DMFC is getting more and more attention as a replacement for secondary batteries. DMFCs have near term market penetration potential in this area with transport being the longer term goal [2]. However, to use methanol in fuel cells commercially, some serious technological challenges like the sluggish kinetics of methanol oxidation reaction and the crossover of methanol to the cathode must be overcome.

The complete anodic oxidation of methanol is described by:



Thermodynamically, this reaction has quite low equilibrium potential (0.016 V versus standard hydrogen electrode, SHE at 25 °C) [3]. But the oxidation of methanol requires a large overpotential, i.e. 0.2–0.4 V depending on the catalyst and operating conditions [4]. The complete oxidation of methanol requires the transfer of six electrons, resulting in sluggish kinetics even on PtRu, the widely accepted best catalyst available for the reaction. Therefore, it is important to investigate the mechanism of

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Table 1
Specification of four different MEAs used in the work

MEA	Anode	Cathode	GDL	Membrane	Applied temperature and duration
IRD	PtRu (1:1) (Johnson Matthey); $\sim 2 \text{ mg cm}^{-2}$	$\sim 56\%$ Pt/C (Johnson Matthey)	Toray TGPH090	Nafion 117	$\sim 140^\circ\text{C}$; 5 min
JM	PtRu (1:1) (Johnson Matthey); $\sim 1.5 \text{ mg cm}^{-2}$	$\sim 20\%$ Pt/C (E-TEK); 2 mg cm^{-2}	Toray TGPH090	Nafion 117	$\sim 130^\circ\text{C}$; 5 min
Flame	PtRu (1:1); $\sim 1.5 \text{ mg cm}^{-2}$	$\sim 20\%$ Pt/C (E-TEK); 2 mg cm^{-2}	Toray TGPH090	Nafion 112	$\sim 140^\circ\text{C}$; 5 min

this reaction on PtRu for increasing the noble metal utilization as well as designing novel catalysts for the reaction.

It is well known that methanol electrooxidation involves several reaction steps with different rates; electrochemical impedance spectroscopy (EIS) can distinguish processes with different time constants, and with this method it might be possible to distinguish different elementary steps of the reaction [5,6]. Although several studies have used EIS to investigate methanol electrooxidation [7–16], to our knowledge only three reports have focused on the mechanistic aspects of methanol oxidation in a DMFC using nanoparticulate catalysts [7,8,16]. Impedance analysis of methanol oxidation in a ‘real world electrode environment’ is important not only to have a clearer understanding of the reaction at the three-phase region, but also to avoid artifacts arising from anion adsorption which results from electrolytes like H_2SO_4 which contains mobile anions [17]. Jiang and Kucernak have reported that the discharge of methanol on Pt is shifted to more negative potentials when Nafion is used as electrolyte instead of H_2SO_4 . They attributed the phenomenon to the absence of mobile anions in Nafion [18]. Moreover, it has also been reported that Nafion coating greatly enhances the methanol oxidation activity on Pt [19]. For the analysis of methanol electrooxidation reaction in this work, we used a single cell fuel cell setup with DMFC membrane electrode assembly (MEA) consisting of a nonparticulate PtRu anode. Besides the mechanistic aspects, using impedance analysis on an MEA could produce important information on protonic conductivity of the catalyst layers [20], and membrane [21]; dependence of the membrane resistance on humidity and temperature [22]; thickness of the catalyst layer [23], etc. We have performed a detailed analysis of the methanol oxidation at the PtRu nanoparticulate anode of a state of the art commercial DMFC MEA both below and above the onset potentials. The impedance data along with the voltammetric measurements were used to obtain an in-depth mechanistic understanding. Finally, the findings were applied for investigating and comparing methanol oxidation performance of different in-house prepared MEAs to the commercial one.

2. Experimental

The electrochemical measurements were performed in a single cell test fuel cell described elsewhere [13]. Three different MEAs were used in this work. One type of MEA was the state of the art product obtained courtesy of IRD Fuel Cells A/S. This MEA, referred to as IRD for the rest of the article, was used for the detailed mechanistic investigation of methanol oxidation and establishing a basis for performance comparison between differ-

ent MEAs. The second MEA, named as JM for the purpose of this article, was fabricated in-house by using an unsupported Johnson Matthey PtRu catalyst (1:1 atomic ratio, 1.5 mg cm^{-2}) as the anode. The cathode was a 20% Pt/C (E-TEK) painted on gas diffusion layer (GDL). The third MEA, named Flame, consisted of an anode synthesized by Flame pyrolysis with a loading of 1.5 mg cm^{-2} PtRu (1:1 atomic ratio). The fabrication of the Flame MEA has been discussed in detail in our previous article [13]. The geometric surface areas of the electrodes for all the three MEAs were 3.14 cm^2 and currents were normalized with the geometric area unless otherwise mentioned. Table 1 summarizes the specifications of the three different MEAs used. The anode of the fuel cell was fed with methanol solutions of different concentrations at a flow rate of 1 ml min^{-1} . The cathode, which also acted as a dynamic hydrogen electrode (DHE), was fed with H_2 [13,17,24]. All the potentials reported in this paper are given relative to a DHE. Two electrode impedance measurements of methanol oxidation in a fuel cell anode have been reported first by Müller et al. [8,25]. The reaction at the dynamic hydrogen electrode is as follows:



In fuel cell research, this reaction is considered very fast compared to reactions like methanol oxidation or O_2 reduction. Because of this the impedance of the DHE can be considered negligible compared to the impedance of the anode side where methanol electrooxidation is occurring. The total impedance of the cell which is the sum of the anode impedance and the cathode impedance can be taken as the impedance of the anode side alone. In fact this assumption has been confirmed experimentally by Diard et al. [16]. The impedance measurements were taken from 100 kHz to 10.5 mHz by applying a sine wave of rms of 10 mV on top of the bias potentials with the potentiostat Parstat 2273 (Princeton Applied Research). The spectra were obtained in two different ways. For the mechanistic investigation, where it was necessary to obtain a huge number of spectra, single sine (100 kHz to 1 Hz) followed by a multi-sine (1.03 Hz to 10.5 mHz) technique was used. Using multi-sine techniques for obtaining low frequency data makes the process significantly faster. Melnick and Palmore [14,15] have also used the combination of single and multi-sine techniques to obtain impedance data for methanol oxidation on Pt. The single sine method for the whole range was used when spectra were measured for the purpose of performance comparisons between different MEAs. During impedance measurements, the perturbation was applied after taking the electrode to the bias potential and waiting for 1 min to establish a pseudo-steady

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