

Electrocatalysis in Direct Methanol Fuel Cells
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Introduction

In 2006, Nobel prize winner George Olah wrote a book in which he proposed a “Methanol Economy” as an alternative to the more popular Hydrogen Economy. Due to its simple chemical structure (methanol is the simplest alcohol), its ease of transport (methanol is liquid at standard conditions), and its high energy density (roughly 20 MJ/kg), methanol is a promising alternative fuel of the future. Although methanol and other alcohols have been used as fuels for over a century, interest in methanol fuel has picked up significantly since Olah’s book was published. Although there are a wide range of aspects of the proposed Methanol Economy, the most research and development regarding the use of methanol fuel is currently focused on Direct Methanol Fuel Cells (DMFC).

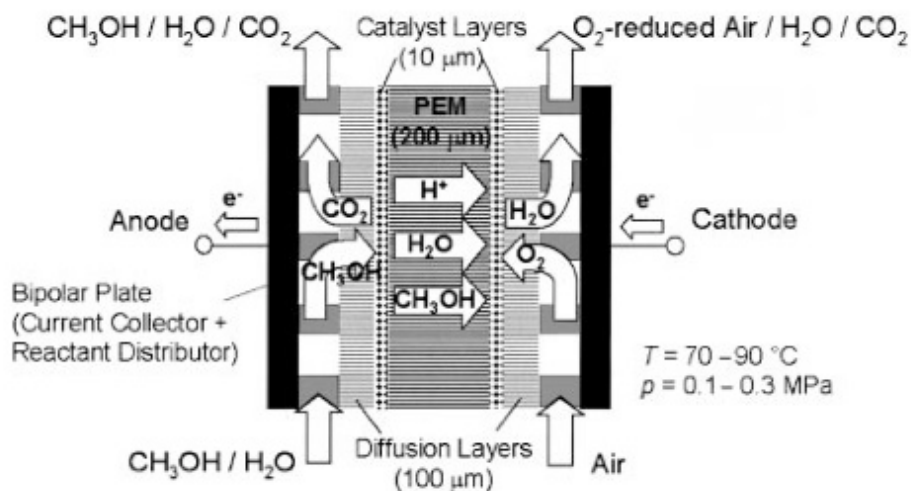
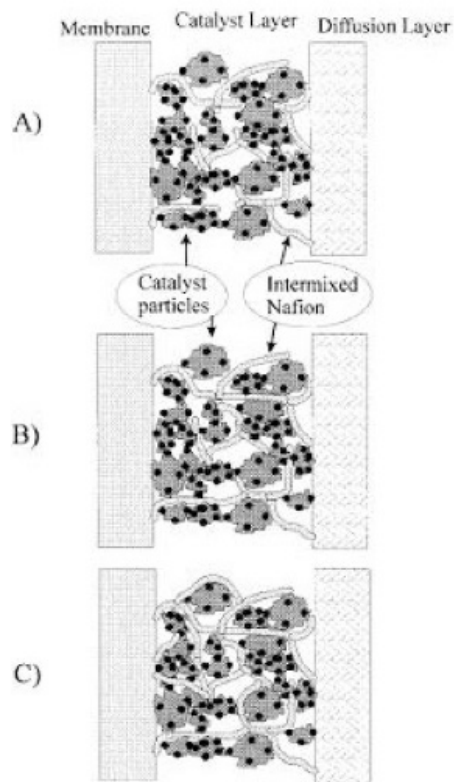


Figure 1: Electrocatalytic Redox Reactions in a Direct Methanol Fuel Cell
Image from Zhou, 2001.

The term “direct” refers to the fact that these cells do not reform methanol to obtain hydrogen for conventional hydrogen PEM fuel cells, but rather they use the methanol directly, without the need for any separate reforming. Although the concept of direct methanol fuel cells has been known for over 40 years, research laboratories continue with rigorous R&D today. Today, DMFCs are not publicly for sale at a large scale, but some speculate that widespread use of the technology is in the near future, particularly as a replacement for batteries in consumer electronic devices such as cell phones, entertainment stations, PDAs, and laptops. Several large consumer electronics companies have shown their prototypes of DMFC-powered consumer electronic devices at electronics shows in recent years. In particular, the U.S. military is said to be field-testing DMFC-powered devices for backup power.

Catalyst Materials and Electrocatalyst Fabrication

By far, the most commonly used catalyst material used for DMFCs is Platinum (Pt). Other metals that have been investigated as electrocatalysts for DMFCs include Ru, Rh, Sn, Fe-Mo, Au, Ni, and Cr. In general, Pt or Pt/Ru catalysts are used at the anode for the oxidation of methanol, and Pt catalysts are used at the cathode for the reduction of oxygen. Unlike other types of supported metal catalysts that usually use a metal oxide (e.x. Al_2O_3) as a support, DMFC catalysts usually use Carbon Black / Activated Carbon as the support. There is also a significant amount of research investigating the performance of carbon nanotubes as the catalyst support (Sun, 2008). The way in which these electrocatalysts are engineered is rather unique and specific to fuel cells.



**Figure 2: Electrical Conduction Bridges of Nafion® Ionomer
Image From Krishnamerthy, 2008**

Electrocatalysts are named as such due to their dual nature as being both electrodes and catalysts. In other words, the material is used not only to reduce the activation energy of the chemical reaction, but also to conduct the electrons that result thereof. There are several ways to make the raw catalyst materials, and several ways to create the electrocatalyst layers over the polymer membranes. Commonly, the catalyst material is purchased as a powder from a manufacturer. Alternatively, the catalyst materials can be made in the laboratory using a technique such as ultrasonic irradiation. Ultrasonic irradiation uses extremely high temperatures and pressures (~ 5000 K, 1000 atm) that appear during the violent cavitations of bubbles to initiate reactions that turn metal ions into metal nanoparticles (Kim, 2009). The catalyst powder, which is typically

Pt over a Carbon support, is then mixed with deionized water, a solvent/dispersion agent such as isopropyl alcohol, and Nafion[®] ionomer solution. The ionomer provides an electrical connection throughout the catalyst particles, as shown in Fig. (2). The catalyst ink is then sprayed or brush-painted onto the polymeric membrane, which is often also made by Nafion[®]. The three layers (anode, membrane, cathode) are then hot-pressed together, forming what is known as a membrane electrode assembly (MEA).

Reaction Kinetics and Mechanisms

The central electrochemical reactions of the DMFC are illustrated in Fig. (3). The overall mechanism, shown in Fig. (3 c), has been known for at least forty years (Veilstich, 1965). And although the mechanism of oxygen reduction at the cathode is simply the reaction shown in Fig. (3 b), the methanol oxidation mechanism Fig. (3 a) is still not completely understood (Kulikovsky, 2007).

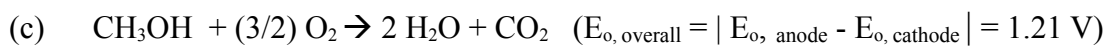
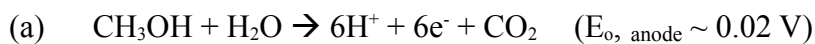


Figure 3: DMFC Electrochemistry. Oxidation of methanol occurs at the anode (a), reduction of oxygen occurs at the cathode (b), and the overall reaction produces around 1.2 V (c).

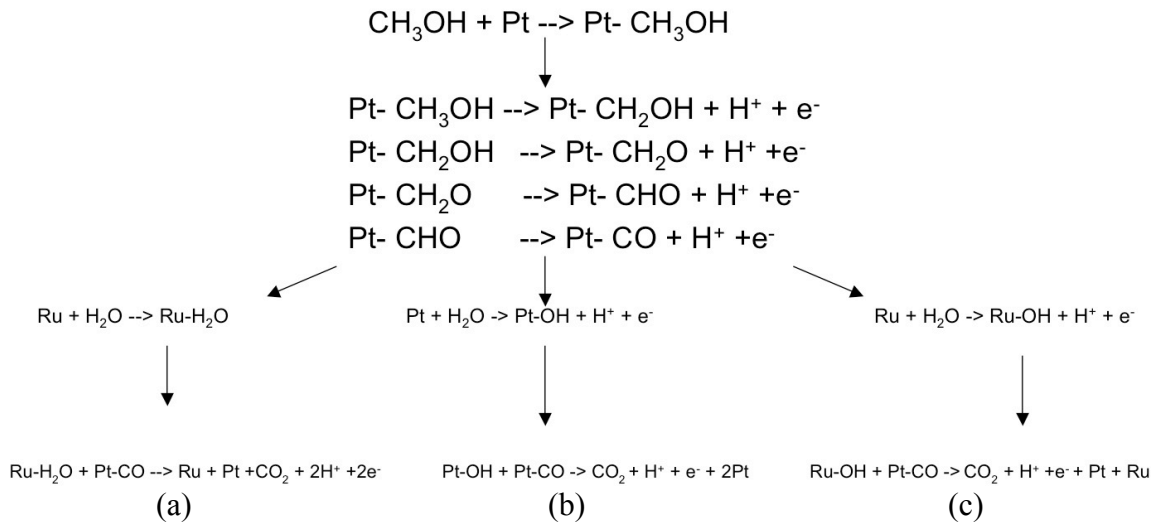


Figure 4: Three Proposed Oxidation Mechanisms with Similar Initial Steps
Note that the reaction shown in Fig. (4 b) proceeds over Pt, but the others proceed via Ru in the final steps.

Three well-known proposed mechanisms for the oxidation of methanol are shown in Fig. (4). These reactions were shown by Gilman, Hogarith, and Brandon, respectively. In all three cases, the reaction proceeds via (1) methanol adsorption, (2), C-H bond activation, (3) water adsorption, and (4) CO oxidation. An alternative reaction mechanism for Pt/Ru catalysts, proposed by Zhao in 2000, is shown in Fig. (5). Unlike the mechanisms by Gilman and Brandon for Pt/Ru methanol oxidation, the mechanism proposed by Zhao requires three sites for adsorption. Also, unlike the others, it involves a COOH intermediate.

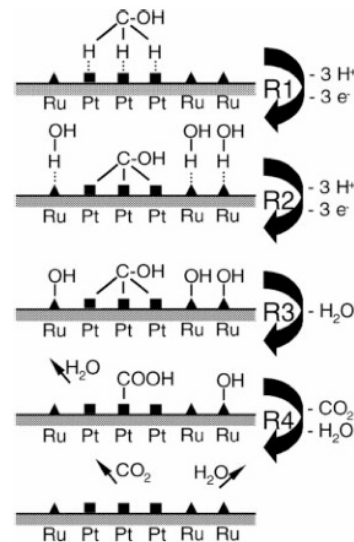
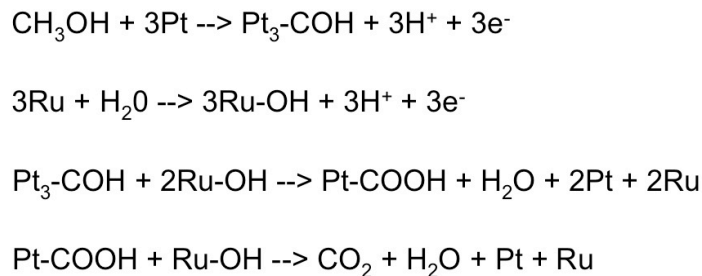


Figure 5: Pt/Ru Methanol Oxidation Mechanism Proposed by Zhao, 2001

Perhaps the most often cited reaction mechanism for methanol oxidation over a Pt catalyst is the so-called “Dual-Path” mechanism, shown below in Fig. (6). It should be noted that for all of the reaction mechanisms discussed, there are always a total of 6 H⁺ and 6 e⁻.

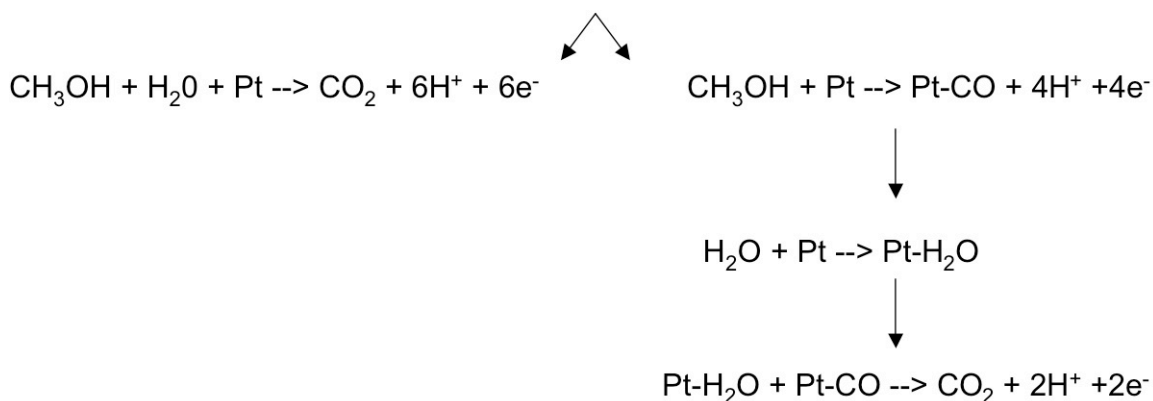


Figure 6: Dual-Path Mechanism for Methanol Oxidation over Pt (Herrero, 1995)

The single most important factor that has prevented mass commercialization of the DMFC is the slow reaction kinetics at the anode and cathode of the cell. The most intensively researched problem of the DMFC kinetics has to do with “methanol

crossover,” during which the methanol passes directly through the membrane and reacts at the cathode, causing a short-circuit in the cell and reducing the cell voltage dramatically. A significant portion of current DMFC R&D seeks to mitigate the problem of methanol crossover, usually by chemically modifying the membrane before the catalyst is applied.

Methanol crossover is typically measured using in-situ spectroscopy to detect the presence of CO_2 at the cathode. In addition to methanol crossover, the electro-osmotic drag of water across the membrane (by H^+ ions) inhibits active sites at the cathode. Another complication of the reaction kinetics, and one that is rarely discussed, is the possibility of oscillatory and chaotic reactions, which has been found during the oxidation of methanol. Period-doubling bifurcations during methanol oxidation were found by Okamoto in 1997, as shown in Fig. (8). In fact, there are several nonlinear aspects of the DMFCs in addition to the reaction kinetics (Zhao, 2001).

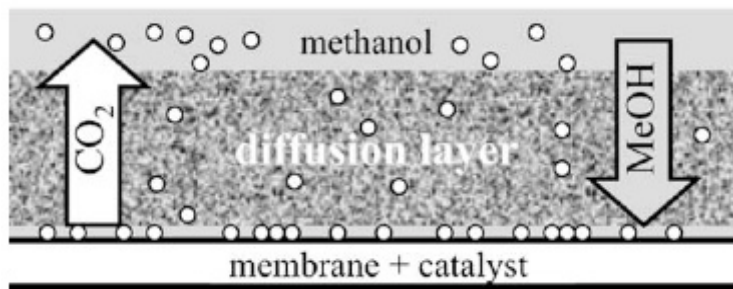


Figure 7: Mass Transfer Requirements in Diffusion Layers (Oedegaard, 2004)

Some other factors influencing the reaction kinetics are the quality of the cell diffusion layer and the geometry of the current-collectors/fuel supply. The DMFC diffusion layers, which are typically made out of carbon paper, provide a medium for mass transport of reactants to and from the electrocatalyst layer. The geometry of the current-collectors is also important, since it forms the pathway of the reactants to the

diffusion layer and the MEA. Recently, current collectors using fractal geometry have been considered. All the factors mentioned above affect the kinetics of the overall reactions.

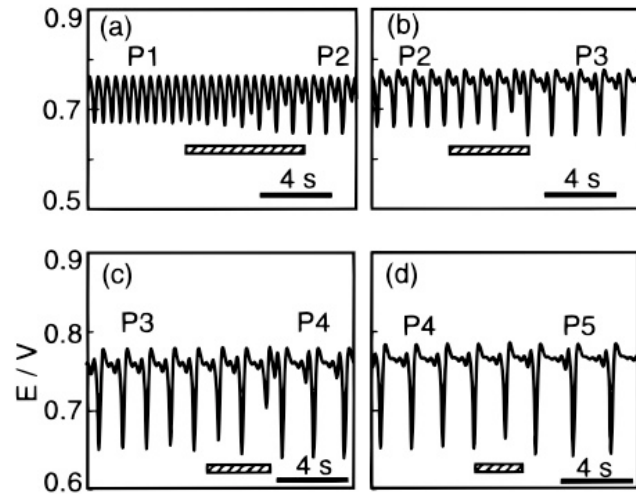


Figure 8: Oscillatory Dynamics of Methanol Oxidation (Okamoto, 1997)

Future Research and Development

There is much future work to be done regarding the electrocatalysis of the DMFC. Improvements in the understanding of DMFC kinetics, materials, and dynamics are likely to continue, given that the current amount of interest in the field is quite high. One interesting idea that has been proposed is direct alkaline methanol fuel cells (DAMFC), in which anions are transferred instead of cations. Before DMFCs play a major role in the automotive economy, they will have to increase power output by approximately six-fold. Although many see that scenario as a likely one, for now all eyes are on small consumer electronics, where DMFCs are arguably on the verge of breaking through into the public market.

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