Fuel cell electrocatalsis : oxygen reduction on Pt-based nanoparticle catalysts

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Chapter 1

Introduction

In this chapter a short introduction on Fuel cells will be given, starting with their history, continuing with their applications and finishing with the challenges. The aims of the thesis will be presented within this framework of challenges and opportunities.

1.1 History of Fuel Cells

For the past decade, oil prices have been climbing to incredible heights. The cost of petrol at the pump is, for most people, the most noticeable manifestation of the price we pay for our energy. When necessities get more expensive it usually sparks interest in alternative ways to obtain the same goal; in this case it renewed the interest in alternative energy conversion devices, such as fuel cells. [1]

Fuel cells were a direct result of the discovery of water electrolysis in 1789 by Adriaan Paets van Troostwijk and Jan Rudolph Deiman. The discovery of the fuel cell itself is usually attributed to Schönbein or Grove, depending on which reference one consults [2]. Regardless of to whom the actual invention can be ascribed to, their discoveries were published months after one another, which means that 1839 is the year in which the concept of the fuel cell was first published. Over the years interest in fuel cells has waned, especially due to the emergence of fossil fuels and the combustion engine. Starting with the oil crises in the 1970's, interest in fuel cells has increased again in recent years. Initially, fuel cells were especially of interest for situations where normal combustion engines (or, in a previous era, steam engines) could not operate, or remote areas which were not connected to the power grid [2; 3]. This includes submarine and space applications. In the last few decades, automotive applications for the general public have become attractive both for consumers to have an alternative to ever-increasing gas prices, and for governments to reduce carbon emissions and dependence on oil [4]. There is a preferred type of fuel cell for each application, with the Proton Exchange Membrane Fuel Cell (PEMFC) preferred for the use in automotive applications [3; 5]. The higher power density and quick start up due to the lower operating temperature make this fuel cell the first choice for commercial applications such as laptop power and cell phone batteries as well [5]. However, the fuel in these cells will differ depending on the proposed applications. For use in vehicles, hydrogen is preferred, due to its high power-density and higher operating potentials. The difficulty in storing this gas makes it less suitable for smaller applications like the previously mentioned laptops and cell phones. For those applications, liquid fuels such as methanol (direct methanol fuel cell DMFC), formic acid (direct formic acid fuel cell DFAFC) or ethanol (direct ethanol fuel cell DEFC) are preferred. The nomenclature of these fuel cells includes "direct" to stress that the respective fuels are used directly, and not reformed to hydrogen before use in the cell. Finally, for large stationary applications, Solid Oxide Fuel Cells [2; 6] are preferred, both because they are easier to adapt to existing infrastructure [1] and can operate at higher current densities. [2]

1.2 Working principle of a Fuel Cell

The operation of a fuel cell is in essence very straightforward, see figure 1.1. Fuel (in the figure represented as hydrogen) is oxidized on the anode, separated by an electrolyte from the cathode, at which oxygen is reduced. The electrical current that will flow in the external circuit can then be used for power generation.

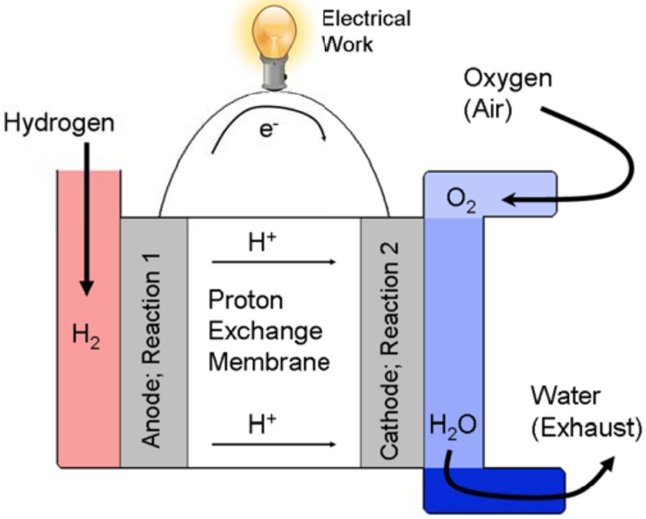

Figure 1.1. Schematic view of a hydrogen-fueled PEM fuel cell in operation.

The basic half-cell reactions for a hydrogen-powered fuel cell are:

$\mathbf{H_2 \leftrightharpoons 2H^+ + 2e^-}$ **Reaction 1.1** $\mathbf{E_0 = 0\ V}$

$\mathbf{O_2 + 4H^+ + 4e^- \leftrightharpoons 2H_2O}$ **Reaction 1.2** $\mathbf{E_0 = 1.23\ V}$

which combine to give the overall reaction:

$\mathbf{2H_2 + O_2 \leftrightharpoons 2H_2O}$ **Reaction 1.3** $\mathbf{\Delta E_0 = 1.23\ V}$

This is, of course, the reverse of water electrolysis.

Reaction 1 is the Hydrogen Oxidation reaction (HOR), which is the reverse of the Hydrogen Evolution Reaction (HER). Both the HOR and the HER have been investigated extensively [7-13], with platinum the most widely used catalyst. [14] The Oxygen Reduction Reaction (ORR) is shown by reaction 2 and has gained significant interest in the past decades as it is currently the efficiency-limiting reaction in a hydrogen-powered fuel cell [15-29]. The equilibrium potential of the HOR at a Pt electrode in the electrolyte is 0V by definition; this is the reversible hydrogen electrode (RHE). The equilibrium potential of the ORR on Pt is at 1.23 V versus the RHE. The pH-independent RHE scale is used throughout this thesis to avoid pH effects on the reference potential.

The difference between the respective equilibrium potentials of the anode (HOR) and cathode (ORR) reactions will be the maximum cell voltage. With multiple of these single cells stacked, the desired power output can be achieved, which is in the order of 100 kW for a fuel cell powered car [30]. The elegance in the operation lies in the absence of greenhouse gas emissions when clean hydrogen is used as fuel (with water as the only product, see figure 1.1 and reaction 1.3), as well as the theoretically high efficiency of a fuel cell [3-5]; gaining the most energy from the fuel. Hydrogen offered commercially at present is often obtained from steam reforming, and has small amounts of carbon monoxide present as contamination. This CO has a negative effect on the performance due to catalyst-poisoning and it will oxidize to CO_2, a greenhouse gas.

There are of course some engineering challenges for fuel cell development as well. The polymer electrolyte membrane has to be improved to reduce resistance and reactant crossover. [16; 31] The crossover current density originates from fuel passing unreacted through the membrane to react at the cathode. Reactant crossover is a major problem as it effectively short-circuits the cell (since Pt is active for both the oxidation and reduction reactions of the cell), reducing efficiency. Furthermore, in case of a DMFC, methanol crossover will poison the cathode. [32-35] Electrolyte resistance, due to the polymer membrane and ionomer content [16; 36], is usually compensated for in membrane electrode assemblies (MEAs) when screening for catalyst activity to verify that the effect observed is due to the catalyst and not to the resistance in the stack. In the operational fuel cell stack, however, resistances must be kept to a minimum, to avoid cell output losses due to resistance. [16; 37] A second problem lies in the carbon that is generally used to support the nanoparticles. The carbon support also causes resistance in a fuel cell [38-40], and particles supported on it are known to dissolute from the catalyst layer [40-42] or sinter into bigger particles, thereby losing their unique properties. [40; 43] One way to avoid this trouble it to manufacture high surface area catalysts that do not rely on carbon supports, such as has been published by 3M [17; 43-45].

1.3 Towards better Fuel Cells

Pt and Pt alloys are currently the best catalysts for the ORR, but even with the best state-of-the-art catalysts there is still a large overpotential, which reduces the total fuel cell output. The overpotential is the potential difference between a thermodynamically determined equilibrium potential of a half reaction and the potential at which this half-reaction is experimentally observed. [46] The overpotential (η) for the ORR in fuel cell systems can be modeled by a Tafel-relation: $\eta = (70 \text{ mV / decade}) \cdot \log(i_{eff})$, where i_{eff} is the effective current density, defined by $i_{eff} = i + i_{crossover}$. [16] The cell loss due to the overpotential for the ORR is limiting the fuel cell efficiency, causing fuel cell stacks to require more individual cells to have the desired power output. With the most active catalyst being Pt, this means a fuel cell stack will become very expensive. One strategy to improve this situation is to find better catalysts, hereby reducing the platinum content in the catalyst, for example by alloying Pt with a second (or multiple) metal. [16; 18; 19; 47-54] Another option is to make better use of the platinum. With the surface of the metal active for catalysis, increasing the surface area to bulk ratio will increase the usage of Pt. Nanoparticles dispersed on high surface area carbon are therefore widely tested. [55-62] Finally, non-precious metal catalysts are of interest to eliminate the platinum availability and cost problem altogether. [18] An order of magnitude increase in the activity versus state-of-the-art carbon-supported nanoparticulate ORR catalysts, and an approximately 5-fold reduction in Pt content is required to meet the cost requirements for large scale automotive applications [51].

1.4 Outline of this thesis

Work for this thesis started at Argonne National Laboratory, in the group of Dr. Markovic, which specializes in oxygen reduction. Chapters 3 through 8 have been prepared there, while experiments for chapter 2 were also performed at Argonne. In the final year, the preparation of chapters 2, 6 and 7, experiments for chapter 8 as well as the assembling of this thesis has been performed at Leiden University.

The testing of catalysts in the actual assembled fuel cell is a time-consuming process [63-65]; therefore bench-top lab testing has been developed by means of the Rotating Disc Electrode in an electrochemical cell. This method, first developed by Schmidt *et al.* [64], is used in this thesis in Chapters 3-7 for nanoparticle electrochemistry. To summarize the process, the catalyst particles are first suspended in water, and then pipetted onto a conductive glassy carbon (GC) disc, which then can be used in the RDE. An added advantage of this setup is that a single half-reaction can be studied in detail, rather than the fuel cell as a whole.

Identical to MEAs, solution resistance will also play a role in measurements in an electrochemical cell, as will be discussed in chapter 2. This chapter also deals with adsorption processes, which are present during the reduction of oxygen in the RDE method. This leads to a superposition of the current due to these adsorption processes on the measured ORR curve. In chapter 2 suggestions for proper compensation for these two RDE-related issues will be given.

In order to contribute to meeting the challenges set out in section 1.3, novel nanoparticulate electrocatalysts were synthesized and measured for their activity towards oxygen reduction. These efforts are illustrated in chapters 3 and 4, where the effects of preparation method and pretreatment on particle size, distribution and segregation profile are shown for solvothermally synthesized Pt_3Co nanoparticles. The Pt_3Co alloy was chosen as this alloy is shown to have increased activity for the ORR in the bulk polycristalline material. [66]

Furthermore, a novel gold core-Pt_3Fe shell catalyst was synthesized in an effort to diminish particle agglomeration, which is discussed in chapter 5. This catalyst has proven to have both increased activity and stability, setting up a way forward to meeting the objectives set out by the United States Department of Energy (DOE) [17].

The nanostructured thin film (NSTF) catalysts from 3M, mentioned before in section 1.2, have shown increased activity and stability for the ORR, and will feature in chapters 6 and 7 of this thesis. The original NSTF, as received from 3M, is a high surface area Pt-based catalyst, which is not supported on carbon. Because it is not carbon-supported, the NSTF catalyst has an increased stability when compared to supported nanocatalysts. [67] In chapter 6, proper catalyst loadings and preparations are determined and a range of NSTFs are measured. From these experiments, PtNi NSTF emerged as the most active catalyst for the ORR. A pretreatment method, which increases both the specific and mass activity of this catalyst, will be discussed in chapter 7.

Due to the fact that the ORR is active at higher potentials in alkaline media than in acid media, alkaline electrolytes are of interest. [68-70] This shows itself in both fuel cells with Alkaline Anion Exchange Membranes (AAEMs) [67; 71; 72] and RDE experiments in alkaline electrolyte. [73] Combining the interest in alkaline media with the finding of chapter 7, where it was shown that the pretreatment method of a catalyst is of importance, chapter 8 deals with the influence of the preparation method on the surface state and electrochemical behavior of Pt (100) in alkaline media. It is shown that the pretreatment has a significant impact on the catalytic activity of the surface. Likewise, the alkali-metal cations, as well as adsorbing anions are shown to have a significant influence on the catalysis by Pt(100).

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