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

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Summary

Work for this thesis started at Argonne National Laboratory (ANL), and in the final year the assembling of this thesis has been performed at Leiden University.

Relevant processes for fuel cells such as the oxygen reduction reaction (ORR) and CO electro-oxidation are studied and described in this thesis. The goal of this research was to find the origin of catalytic activity of Pt-alloys for these reactions, and specifically to use this knowledge to develop new active catalysts for the ORR. In order to effectively pursue this goal, it was necessary to improve the reliability of the comparison between model rotating disk electrode (RDE) experiments and *in-situ* membrane electrode assembly (MEA) testing. Improvement of the RDE method will allow for faster catalyst screening, thereby decreasing the development time. The outcome is extremely useful in the development of fuel cells and reducing the dependence on fossil fuels, while at the same time reducing harmful emissions.

In order to facilitate these goals, several techniques have been applied. First of all, basic electrochemical methods such as cyclic voltammetry (CV) and impedance spectroscopy have been used to study adsorption and reactions on the electrode, as well as the effect of electrolyte resistance. The previously mentioned RDE measurements allowed for effectively reducing the influence of diffusion so that the kinetic activity towards the ORR could be screened for various catalysts. In addition, non-electrochemical supplementary techniques have been applied to confirm catalyst structures. These techniques include *ex-situ* electron microscopy, such as scanning tunneling miscroscopy (STM), scanning electrode microscopy (SEM) and transmission electron microscopy (TEM). Added to this was elemental mapping by high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and Energy-dispersive X-ray scattering (EDX). X-ray diffraction (XRD) was applied as well to observe nanoparticle size, composition and crystallinity.

Theory was used by cooperating groups to support our experimental findings and explain observed trends. Density functional theaory (DFT) calculations were performed by J. Greeley at the center for nanoscale materials at ANL, and Monte Carlo simulation by G.Wang at Purdue University.

The thesis opens in Chapter 2 with a detailed investigation of an intrinsic problem of working with electrically conducting electrolyte: electrolyte resistance. This resistance causes a deviation of the actual potential at the electrode from the applied potential by the potentiostat at higher currents; for example when currents are high due to a reduction in diffusion limitation in a RDE measurement. As this resistance is very different in magnitude from that observed in a MEA, this may lead to differences in interpretation. The chapter further deals with the influence of adsorption processes on the electrode during the ORR in the RDE experiments, another deviation from the steady-state operation of the MEA. As resistance and superimposed adsorption currents are relatively easy to compensate for, after proper compansation has been applied, the RDE method will be more accurate when comparing the data in the following chapters with MEA measurements in the literature.

The oxygen reduction reaction (ORR) on platinum-containing nanoparticles (NPs) is reported in detail in chapters 3-7. Pt_3Co nanocatalysts were synthesized and characterized (chapters 3 and 4), with special care taken of the pretreatment and its effect on particle size and corresponding ORR activity. A volcano-shaped dependence of mass activity depending on particle size was found, due to the opposite trends that for increasing particle size the kinetic current density increases, but the specific surface area per unit mass decreases. The optimal particle size of these Pt_3Co particles is shown to be 4.5 nm.

Novel core-shell particles, dispersed on carbon, are discussed in chapter 5. These particles have a gold core and Pt_3Fe shell and are shown to have not only increased activity for the ORR, but also increased stability due to their lower rate of agglomeration.

Non-carbon supported nanostructured thin film (NSTF) catalysts are discussed in chapters 6 and 7. Chapter 6 deals with the determination of the optimal catalyst loading and determination of ORR activities of non-modified NSTF catalysts, as received from 3M. From the most active catalyst of these results, PtNi NSTF, PtNi nanotubes were created and are shown in chapter 7. This nanotube catalyst has the highest kinetic activity of any nanoparticle catalyst and even though they are of larger size, they have a higher mass activity than small carbon supported high surface area catalysts as well. Added to this increase in catalytic activity is the increased stability, which comes through the lack of carbon support (no support corrosion or particle dissolution) and larger particle size (lower particle agglomeration).

From chapters 3-7 it is clear that the increase in catalytic activity for the ORR comes with a reduced affinity for surface oxidation. This leads to the belief that the observed activity for these highly active catalysts is due to their ability to keep the surface clean from strongly adsorbed oxide-containing species.

The final chapter of this thesis gives an insight on the electrochemical behavior of Pt (100) in alkaline electrolyte. The pretreatment of this reactive surface is the key in the surface structure and the catalytic activity that it displays, just as the pretreatment of the nanoparticle catalysts in chapters 4 and 7 influences their structure and catalytic behavior as well. In contrast to acidic electrolyte, in alkaline media the surface state is more obvious from the adsorption processes that can be seen in the blank cyclic voltammetry. Furthermore, alkali-metal cations are shown to have a significant impact on both adsorption processes on Pt(100) and the catalytic activity for the oxidative stripping of adsorbed carbon monoxide.