Electrocatalysts and their Supporting Materials for Proton Exchange Membrane Fuel Cells: Activity and Durability Studies

This thesis describes investigations conducted exploring the activity, stability and durability of supported nano-particulate, bulk and thin film electrocatalysts used in proton exchange membrane fuel cells (PEMFCs). The effects of different factors and conditions on the reactions involved in oxygen reduction, carbon monoxide and methanol electro-oxidation reactions were explored. Employed catalysts were characterized electrochemically and physiochemically using techniques such as: cyclic voltammetry, rotating disk electrode technique, SEM, TEM, EDX, XPS, TGA/DTA, Raman, XRD, FTIR-IR among other methods. The thesis begins with an introduction in Chapter 1 providing an overview of fuel cells, their associated reaction mechanisms, catalysts and catalysts supports. Chapter 2 presents the theoretical background to the study including equipment and the techniques used to analyse the catalysts. Subsequently examples of electrochemical characterization for electrochemical surface area are given followed by a description of rotation disk electrode (RDE) principles and set-up. Next the determination of oxygen reduction activity and carbon monoxide electro-oxidation voltammetry are described in addition to long-term durability procedures. A significant part of the PhD study involved development of electrochemical instrumentation and techniques, such as: RDE and set-up, oxygen reduction, methanol and CO electrooxidation, long-term durability procedures, etc. The techniques employed by the author were self-taught or learnt by working with experienced collaborators during the first years of the PhD study. In the advanced stages of the project these techniques were employed by the DTU Proton Conductor group on a daily basis. In addition the author attained a high level of proficiency in operating the following instruments: TEM (FEI Tecnai T20 G2), EDX, AFM, XRD (PANalytical Multipurpose Diffractometer) and FTIR-IR. Chapter 3 describes the results of synthesis and testing of the Pt nanoparticulate catalyst supported by PBI wrapped Graphene for oxygen reduction reaction in PEMFCs. The physiochemical material's characterisation, preparation procedures for thin film RDE electrodes, catalyst's ink composition, oxygen reduction reaction activity, electrochemical surface area and durability studies are also described in detail. Finally Chapter 4 presents the results obtained regarding novel, bulk Pt-Si alloy catalysts used in methanol and carbon monoxide electro-oxidation. The work described was conducted in collaboration with The Electrochemical Energy Lab (EEL), Massachusetts Institute of Technology (MIT), U. S. Preparation and structural characterisation methods used for bulk and surface compositions of Pt-Si alloys is also presented. Electrochemical characterisation showed a gradual improvement of activity for carbon monoxide and methanol electro-oxidation when higher Si contents were employed in the Pt-Si alloy. Chapter 5 describes the preparation, material characterisation and initial electrochemical measurements of methanol electro-oxidation for ALD deposited Pt films on Si(100) and Pt-Si alloys on Si(100). ALD deposited Pt films on Si(100) were subsequently annealed at various temperatures to obtain Pt-Si alloy film on Si(100). Obtained alloys were subsequently characterised as potentially highly active methanol electro-oxidation catalysts, based on conclusions from Chapter 4. Chapter 6 consists of concluding remarks and describes prospective future research. Chapter 7 contains Appendixes.