



HELSINKI UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry and Materials Sciences

Annukka Santasalo

Electrocatalysis of organic molecules on platinum catalyst
surfaces: from the fundamentals to the polymer electrolyte
fuel cell applications

Thesis for the degree of Licentiate of Science in Technology submitted for
inspection, Espoo, 9 October, 2009.

Supervisor

Professor Kyösti Kontturi

Instructor

Docent Tanja Kallio



Author Annukka Santasalo	
Title of Thesis Electrocatalysis of organic molecules on platinum catalysts surfaces: from the fundamentals to the polymer electrolyte fuel cell applications	
Abstract <p>Polymer electrolyte fuel cells (PEFC) fuelled with organic compounds can be used as energy sources in small, portable applications due to their high power density. Organic fuels such as low molecular mass alcohols have been studied for these applications due to their uncomplicated and relative safety when compared to gaseous fuels. However, although studied already for decades, the adsorption and oxidation mechanisms are still not well understood which is vital for the development of fuel cell applications. In the literature part electrocatalysis of organic molecules is discussed: the electrode material, ions and molecules in the liquid phase and the electrode potential applied have highest influence on the adsorption and oxidation of these molecules. The probability of a metal to be a suitable catalyst for a certain organic molecule can be estimated by using the molecular orbital theory of both phases.</p> <p>The experimental part includes two published articles and auxiliary experiments with stepped single crystal electrodes. In the first publication, crossover through the Nafion® 115 membrane as a function of time and performance in a PEFC for several organic molecules is studied. Methanol as the smallest uncharged molecules has the highest crossover rate through the studied membrane, however, also it produces superior performance in a platinum ruthenium catalysed PEFC. Even if other molecules do not reach the current densities produced with methanol, the open circuit potential obtained with isopropanol is dramatically higher compared to methanol.</p> <p>Consequently, in the second publication the oxidation of methanol, isopropanol and their mixtures has been studied on platinum single crystal electrodes. On Pt(111) the alcohol mixture produces higher current densities than pure alcohol solutions in acidic electrolytes (HClO₄ and H₂SO₄). As a result stepped single crystals with Pt(111) terraces and steps of Pt(100) or Pt(110) configuration have also been studied. The only stepped surface which produced higher current densities has wide Pt(111) terraces and Pt(100) steps. In addition, the oxidation of 2-propanol and alcohol mixture is studied with IR spectroscopy and the results indicated that both isopropanol and methanol co-adsorbed on the Pt(111) surface, however, the explanation for the higher activity of an alcohol mixture compared to the isopropanol oxidation is still under investigation..</p>	
Supervisor Professor Kyösti Kontturi	Instructor Docent Tanja Kallio
Chair Physical Chemistry	Chair code Kem-31
Pages 56	Language English
Keywords Polymer electrolyte fuel cell, electrocatalysis, oxidation of alcohols	Date 9 th October 2009



Tekijä Annukka Santasalo	
Lisensiaatintutkimuksen nimi Orgaanisten molekyylien elektrokatalyyysi platinapohjaisten katalyyttien pinnalla: perusteista polymeerielektrolyyttipolttokennoihin	
Tiivistelmä <p>Orgaanisia polttoaineita käyttäviä polymeerielektrolyyttipolttokennoja (PEPK) voidaan käyttää energianlähteinä pienissä, kannettavissa sovellutuksissa korkeiden tehotehoksiensä vuoksi. Nestemäiset polttoaineet kuten alkoholit ovat kiinnostavia polttoaineita kuluttajasovellutuksiin, koska ne ovat turvallisempia ja helpompia käyttää kuin kaasumaiset polttoaineet. Vaikka orgaanisia polttoainevaihtoehtoja on tutkittu jo vuosikymmeniä, niiden adsorptiota ja hapettumista platinakatalyyttien pinnalla ei vielä tunneta kunnolla, mikä on edellytyksenä käytännön sovellusten suunnittelussa. Työn kirjallisessa osassa käsitellään orgaanisten molekyylien elektrokatalyyysiä eli niiden adsorboitumista sekä hapettumista erilaisille platinakatalyyttipinnoille. Näihin ilmiöihin vaikuttavat erityisesti valittu elektrodimateriaali, liuoksissa olevat ionit ja molekyylit sekä elektrodin potentiaali, joiden matemaattisia tarkasteluja voidaan käyttää hyväksi arvioitaessa elektrodimateriaalin soveltuvuutta tietyn orgaanisen aineen elektrokatalyyysiin.</p> <p>Kokeellinen osa koostuu kahdesta julkaistusta artikkelista sekä lisämittauksista yksikide-elektrodeilla. Ensimmäisessä artikkelissa on tutkittu erilaisten orgaanisten, pienimolekyyli-massaisten komponenttien kulkeutumista paljon käytetyn Nafion® 115 membraanin läpi ajan funktiona sekä näiden polttoaineiden suorituskykyä PEPK:ssa. Metanoli pienikokoisimpana, varautumattomana molekyylinä kulkeutui nopeitten tutkitun membraanin läpi, mutta sillä saatiin korkeimmat virrantiheydet platina-ruteniumkatalysoidussa polttokennossa. Vaikka muut molekyylit eivät saavuttaneet metanolin kaltaisia virrantiheyksiä, isopropanolilla saavutettiin metanolia huomattavasti korkeampi avoimen virtapiirin jännite.</p> <p>Toisessa julkaisussa on näiden tulosten pohjalta tutkittu metanolin, isopropanolin sekä niiden muodostaman seoksen hapettumista elektrodeilla, joiden pinta-atomit ovat järjestäytyneet yhden kiderakenteen mukaisesti. Korkeimmat virrantiheydet alkoholiseokselle kummassakin happamassa elektrolyytissä saatiin Pt(111) kidepinnalla, joten lisämittauksia suoritettiin elektrodeilla, joilla oli Pt(111) suuntautuneet terassit sekä Pt(100) tai Pt(110) suuntautuneet askelmat. Tämän lisäksi 2-propanolin sekä alkoholiseoksen hapettumistuotteita tutkittiin infrapunaspektroskopiolla, jolla havaittiin että molemmat puhtaat alkoholit alkoholiseoksesta sekä adsorboituvat että hapettuvat Pt(111) pinnalla. Valitettavasti selvyttä siihen miten alkoholiseos edesauttaa isopropanolin hapettumista, ei näillä mittausmenetelmillä saatu.</p>	
Työn valvoja Professori Kyösti Kontturi	Työn ohjaaja Dosentti Tanja Kallio
Professuuri Fysikaalinen kemia	Koodi Kem-31
Sivumäärä 56	Kieli Englanti
Avainsanat Polymeerielektrolyyttipolttokenno, elektrokatalyyysi, alkoholien hapettuminen	Päiväys 9.10.2009

Preface

The experiments for the publications have been performed at the Research Group of Physical Chemistry and Electrochemistry, Helsinki University of Technology between July 2006 and December 2007 and at Universidad de Alicante, Spain at time period January – June 2008. The writing process for the publications and this thesis has been carried out from since at Finland. The financial possibility to travel and work in Spain has been provided by Finnish cultural foundation and Helsinki University of Technology and is gratefully acknowledged.

First I would like to address my gratitude for Prof. Kyösti Kontturi for providing me an opportunity to start my PhD studies with fuel cell topic and for all help he has given me at the founding process for my exchange period in Spain. My supervisor Dr. Tanja Kallio I would like to give my sincere gratitude for filling me up with ideas and offering her guidance also from a distance. I would like to thank all other staff members of the laboratory especially other PhD students for filling up the coffee room and being there for me when the help was urgently needed.

Secondly I would like to thank Prof. Juan Feliu for the opportunity to work for half a year in Spain and my supervisors Dr. Fran Vidal-Iglesias and Dr. Jose Solla-Gullón for introducing me into the world of electrocatalysis and single crystal electrodes; slowly but firmly in Spanish with a lot of patience. I would also like to address my special thanks for my lunch group for providing me company at the long hours of Spanish *almuerzo* and *comida*.

This work could not have been performed without a strong support of my family and friends in all my choices. Finally, I would like thank my wonderful fiancé Matti for inventing the interesting idea of working abroad and travelling between France and Spain.

Otaniemi 9th October 2009

Annukka Santasalo

List of Symbols

c	concentration	mol
e	charge of a proton	$0.16027 \times 10^{-18} \text{ C}$
E	electrode potential	V
E_{OCP}	open circuit potential	V
E_{PCZ}	electrode potential at the potential of zero charge	V
F	Faraday's constant	96485 C mol^{-1}
n	number of the electrons	
z	charge number	
θ	surface coverage	
μ	chemical potential	J/mol
Φ	work function	eV
ϕ	inner potential (Galvani potential)	V
χ	surface potential	V
ψ	outer potential	V

List of Abbreviations

2-PrOH	Isopropanol
CB	Conduction Band
DEMS	Differential Electrochemical Mass Spectroscopy
DMFC	Direct Methanol Fuel Cell
fcc	Face centred cubic
hkl	Miller indices
HOMO	Highest Occupied Molecular Orbital
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
MEA	Membrane Electrode Assembly
MeOH	Methanol
OCP	Open Circuit Potential
OLEMS	On-Line Electrochemical Mass Spectroscopy
Pt[n(111) x (100)]	Platinum stepped single crystal electrodes with Pt(111) terraces and Pt(100) steps.
Pt[n(111) x (110)]	Platinum stepped single crystal electrodes with Pt(111) terraces and Pt(110) steps.
PEFC	Polymer Electrolyte Fuel Cell
PZC	Potential of Zero Charge
RHE	Reversible Hydrogen Electrode
SCE	Single Crystal Electrode
SSCE	Stepped Single Crystal Electrode
VB	Valence Band