"Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells"

Edited by Zhen-Xing Liang (South China University of Technology, Guangzhou, China) and Tim S. Zhao (The Hong Kong University of Science and Technology, Hong Kong), RSC Energy and Environment Series, No. 6, The Royal Society of Chemistry, Cambridge, UK, 2012, 264 pages, ISBN: 978-1-84973-405-9, £153.99, US$246.00

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"Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells" is aimed at a general audience with an interest in low power fuel cells, as well as experts in the area. The book is edited by Zhen-Xing Liang, Lecturer at the South China University of Technology, and Tim S. Zhao, Professor of Mechanical Engineering at the Hong Kong University of Science and Technology (HKUST) and director of the HKUST Energy Institute. The book contains seven chapters in 264 pages and reviews the catalysis of alcohol electrooxidation in low-temperature fuel cells. The reader will find a general overview of the catalysis involved in the oxidation of alcohols such as methanol and ethanol. More unusually the oxidation of ethylene glycol and glycerol are also described in detail. Although the title for this book is specific to alcohol fuel cells it also contains individual chapters describing the oxidation of other fuels of interest such as formic acid, borohydride and sugars. The book concludes with a chapter on the challenges that alcohol fuel cells need to overcome.

Role of the Platinum Group Metals

Many of the book's chapters are easy to read even for people with little experience in the area. Chapter 1, 'Electrocatalysis of Alcohol Oxidation Reactions at Platinum Group Metals', by Claude Lamy (University of Montpellier, France) and Christophe Coutanceau (Université de Poitiers, France), starts with a good if simplistic overview about what constitutes fuel cell efficiency. This is an important subject and the authors' general description can easily be followed by students in chemistry or related subjects. The authors highlight that the theoretical efficiencies for methanol/air and ethanol/air fuel cells are actually higher than hydrogen/oxygen fuel cells. This is a great foundation for the book because it really justifies the need for research in this area. The chapter continues with a very simplistic description of the methods used for the synthesis and characterisation of fuel cell catalysts, from well-known chemical and electrochemical approaches to more exotic methods such as plasma-enhanced techniques. The content flows in a logical order with this introduction followed by dedicated sections describing in detail the oxidation of different fuels. The oxidation of methanol or ethanol is described in acidic environments, mainly for the well-known platinum-based binary catalysts PtM/C (M = ruthenium or tin), at different atomic ratios.

The authors describe the differences in reactivity when using different atomic ratios such as $Pt_{0.5}Ru_{0.5}$, $Pt_{0.8}Ru_{0.2}$, Pt_3Sn and Pt_9Sn. These binaries are known to be active because of the efficient removal of adsorbed carbon monoxide (*via* the bifunctional mechanism), a common intermediate in the oxidation of primary alcohols. In contrast, the oxidation of ethylene glycol and glycerol is described mainly in alkaline media with the authors focusing on the use of carbon supported platinum, platinum-palladium and platinum-palladium-bismuth for the oxidation of ethylene glycol and platinum, palladium and gold catalysts and their binaries and ternaries such as PtPd, PtBi, PdBi and PtPdBi for the oxidation of glycerol. The chapter offers a good introduction, although it lacks references to the use of commercial catalysts for methanol oxidation (1, 2).

Catalyst Preparation

Chapter 2, 'Nanoalloy Electrocatalysts for Alcohol Oxidation Reactions', by Jun Yin (Cornell University, New York, USA) *et al.* describes the use of PtAu catalysts for alcohol oxidation. The synthesis of PtAu catalysts is a very interesting topic with challenging nanoscale catalyst preparation. Nanoscale gold has been shown to produce surface oxygenated species such as gold(III) oxide, adsorbed gold hydroxide or gold(III) hydroxide which are highly active for the

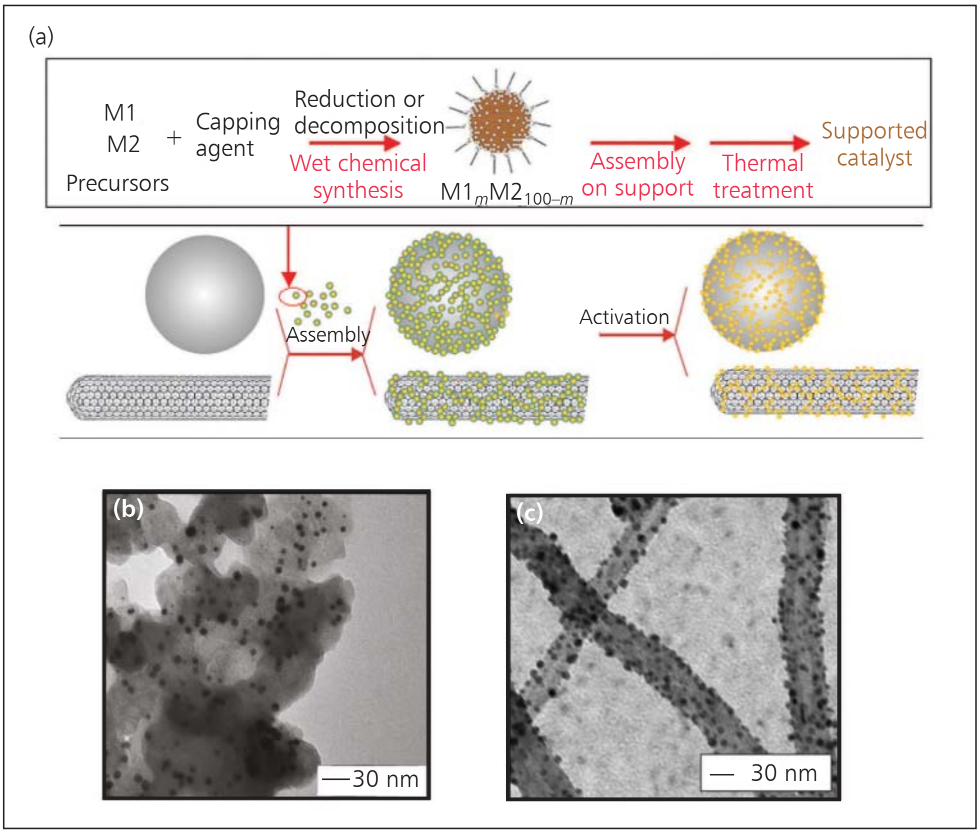

Fig. 1. (a) A general scheme showing the molecularly engineered synthesis of bimetallic nanoparticles capped with a monolayer shell of oleic acid/oleylamine and the preparation of bimetallic nanoparticles supported on carbon powders or carbon nanotubes by assembly and activation. Transmission electron microscopy images showing: (b) $Au_{22}Pt_{78}$ nanoparticles supported on carbon black; and (c) Au nanoparticles supported on carbon nanotubes (Reproduced by permission of The Royal Society of Chemistry)

removal of adsorbed CO, especially in alkaline media. Traditional methods for PtAu catalyst preparation are mentioned such as co-precipitation, impregnation with subsequent reduction, and calcination. More interestingly, the synthesis of Au and PtAu supported nanoparticles *via* the molecular encapsulation synthesis is described (**Figure 1**). This approach involves three steps: (a) chemical synthesis of metal nanocrystal cores with molecular encapsulation; (b) assembly of the encapsulated nanoparticles on support materials; and (c) thermal treatment of the supported nanoparticles. A brief mention of core–shell type PtAu nanoparticles is also included although no characterisation data is shown. PtAu nanoparticles with different atomic compositions are presented for the oxidation of methanol in alkaline and acidic media. An iron(II,III) oxide Fe_3O_4@Au@Pt ternary is presented as a more active catalyst than Pt in acidic media. The chapter finishes with a section dedicated to the characterisation of PtAu particles and includes experimental data from different techniques such as X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) which adds detailed information to help understand the catalysis.

Quantum Mechanical Modelling

Chapter 3, 'Theoretical Studies of Formic Acid Oxidation', by Wang Gao and Timo Jacob (Universität Ulm, Germany), is the only chapter dedicated to the use of quantum mechanical modelling for the understanding of chemical reactions at the molecular level. Although formic acid is not an alcohol, it is of interest in terms of fuel cell efficiency for low power electronics. The authors cover the oxidation of formic acid in ultra-high vacuum conditions and also with increasing water coverage. Importantly, they pay attention to the effect of the electrochemical potential on the formic acid dehydrogenation and include a detailed discussion of the adsorbed products that are formed. A detailed and informative discussion of the different reaction pathways, direct and indirect, is presented. Readers with some experience in the field will find the content extremely interesting. It is slightly disappointing that the editors did not include more content towards the use of theoretical modelling for the oxidation of alcohols.

Catalysis by Gold

Chapter 4, 'Gold Leaf Based Electrocatalysts', by Rongyue Wang and Yi Ding (Shandong University, China) is dedicated to the use of nanoporous gold leaf (NPG-leaf) as an alternative catalyst for the oxidation of formic acid and alcohols in alkaline media. The chapter describes the formation of NPG by chemical dissolution also known as dealloying. This is a well-known process and has been applied for many years in the manufacturing of high surface area catalysts. The authors present as an example the formation of NPG from a gold-silver alloy. Selective dissolution of Ag leads to the formation of a porous structure (**Figure 2**) (3). The authors describe the excellent research done by John Newman (University of California, Berkeley, USA) *et al.* (4) and Jonah Erlebacher (Johns Hopkins University, USA) *et al.* (5) and the reader is advised to follow up these references for further, detailed information. Overall NPG-Pt catalysts give very low benefit compared to Pt/C.

In fact, the area of dealloying is currently an on-going research topic aimed at the design of highly active catalysts for the oxygen reduction reaction in H_2/O_2 fuel cells. Experts in the area such as Professor Doctor Peter Strasser, now at Technische Universität Berlin, Germany, have documented very interesting results with the study of dealloyed particles and their use as catalysts for the oxygen reduction reaction (6, 7). However, the use of dealloyed catalysts has not been well documented for alcohol oxidation.

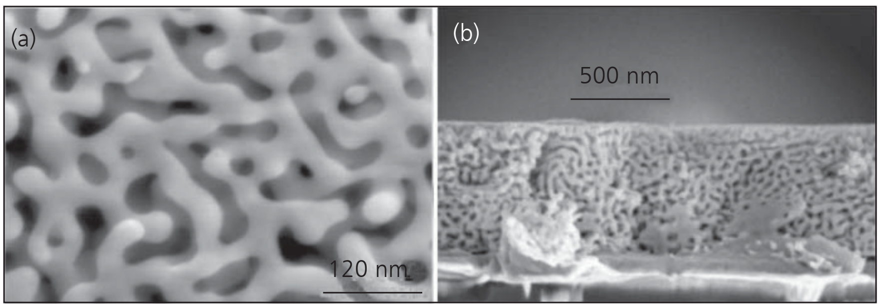

Fig. 2. Scanning electron microscopy images of a nanoporous gold leaf (Reproduced by permission of The Royal Society of Chemistry and (3))

Alkali Metal Borohydrides

Chapter 5, 'Nanocatalysts for Direct Borohydride Oxidation in Alkaline Media' by Christophe Coutanceau *et al*. considers the use of alkali metal borohydrides as fuels. Sodium borohydride is preferred because it offers a compromise between specific energy density and relative abundance. The authors clearly explain the anodic and cathodic reactions that occur in a direct borohydride fuel cell (DBFC) and the theoretical efficiency of a system capable of achieving the 8 electron reaction. Due to the alkaline environment used the catalysts considered are the usual binaries and ternaries, such as PdAu, PdNi and PdPtBi. The authors describe a very interesting study of the kinetics of the electrode reaction but most importantly they present a discussion of what makes a catalyst selective towards complete oxidation and also to the inhibition of hydrogen oxidation. The use of $Pt_{0.9}Bi_{0.1}/C$ is presented as the most selective catalyst that leads to the $8e^-$ pathway without significant hydrogen evolution. Although this anode catalyst led to lower performance compared to Pt/C, in terms of current density, it is of interest for a DBFC because of increased fuel efficiency, a prime parameter for the use of the fuel. It is important to highlight that a system with high cell efficiency is more attractive for many practical applications than a system with low efficiency and high current density. The authors have written a very interesting chapter and this reader gained useful knowledge about the technology.

The Use of Enzymes

Chapter 6, 'Bioelectrocatalysis in Direct Alcohol Fuel Cells', by Holly Reeve and Kylie Vincent (University of Oxford, UK), is dedicated to the use of enzymes for the oxidation of sugars such as fructose, lactose and glucose. The use of sugars for fuel cells is a very interesting area for research since it is based on the generation of electricity by the oxidation of natural products. Actually, the full oxidation of a primary alcohol to carbon dioxide is also possible when using a chain of enzymes *via* a sequence of chemical reactions. This is a key characteristic that differentiates enzymes from metal nanoparticles. For instance, there are very few metal catalysts capable of achieving the full oxidation of dilute ethanol to CO_2 without the formation of incomplete products such as acetaldehyde and acetic acid (8). The authors give a fair and realistic view of the practical problems of enzymes as catalysts due to their relatively large size, which leads to low volumetric density and their limited stability when varying conditions such as pH, temperature, pressure and solvent type. The authors highlight that biofuel cells could have their main application as bioimplantable fuel cells for pacemakers and for the purification of waste water. Although research in this area is in its infancy, the authors give an excellent overview of the use of biofuel cells and the reader with an interest in biocatalysis will find this chapter extremely interesting.

Problems in Alcohol Oxidation

The book closes with Chapter 7, 'Challenges and Perspectives of Nanocatalysts in Alcohol-Fuelled Direct Oxidation Fuel Cells', by Eileen Hao Yu (Newcastle University, UK) *et al*. This chapter covers some of the main problems in alcohol oxidation focusing on the factors affecting activity and stability, including the need for more active catalysts capable of oxidising adsorbed CO. The authors report on the use of binary and ternary catalysts in alkaline and acid media, such as PtRu, PtSn and PtRuM (M = tungsten, molybdenum, nickel) and PtSnM (M = Ni or Ru), PtAu, PdNi and PdIrNi. The use of metal oxides such as cerium(IV) oxide, nickel(II) oxide, cobalt(II,III) oxide and manganese(II,III) oxide as promoters capable of introducing oxygenated species to remove adsorbed CO is also described. A brief mention of the benefits and disadvantages of the use of core–shell catalysts is presented with a special emphasis on PtAu core–shell catalysts. In terms of stability, some interesting approaches are mentioned such as the use of alternative carbon supports (graphene and N-doped carbon nanotubes) and supports such as titanium dioxide and tungsten carbide. The authors, however, do not mention the main problems of anode stability, such as base metal dissolution, membrane contamination and the impact on cathode performance or relate these issues to real fuel cell data.

Conclusion

The authors describe in a detailed manner the electrocatalytic oxidation of primary alcohols and other relevant fuels of interest for low power fuel cells in both acid and alkaline media. The reader gains a useful introduction to the catalysis involved in the oxidation of different fuels, such as methanol, ethanol, ethylene glycol, glycerol, borohydride and sugars. While enzymes and gold catalysts have been introduced, platinum group metal catalysts, especially those based on Pt and Pd, are the state of the art for these technologies. The book only disappoints in some areas such as the lack of real fuel cell data and, for this reviewer's taste, an overemphasis on alcohol oxidation in alkaline media. Overall, this book can be a good starting point for students and researchers with an interest in low power fuel cells.

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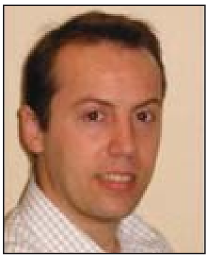
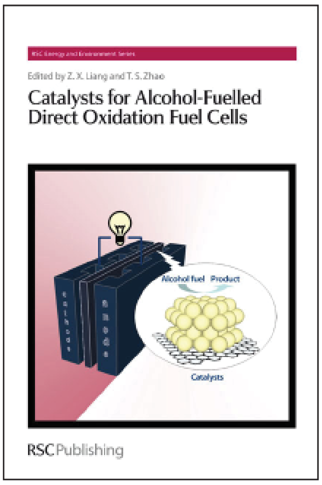


Alex Martinez Bonastre received his PhD from Southampton University, UK, in 2007 and joined the Fuel Cells Research Group at Johnson Matthey Technology Centre, Sonning Common, UK, in 2006, where he is a Senior Scientist. His work centres on the electrochemical characterisation of catalysts and fuel cell components and he is a technical leader in the areas of alcohol and hydrogen fuel cells, working mostly with pgm catalysts.



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