Project no.: NMP3-CT-2004-505906

Project acronym: NENA

Project title: Nanostructures for Energy and Chemicals Production

Instrument: STREP

Thematic Priority: Nanoscience and nanotechnology

Final Publishable Executive Summary

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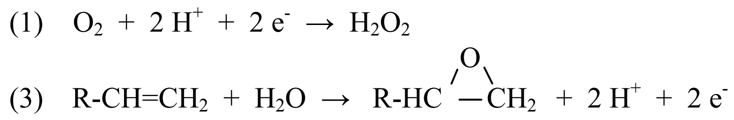
Start date of project: 01.07.2004 **Duration:** 36 months

Project coordinator name: Kyösti Kontturi
Project coordinator organisation name: Helsinki University of Technology

8 Project execution

8.1 Aim of the project

The aim of this project is to develop advanced nanostructured materials and components for the co-generation of chemicals and energy in a fuel cell. Two examples have been chosen for this application, oxygen reduction to yield hydrogen peroxide and double bond electrochemical oxidation to yield epoxides, as shown in scheme 1.



(1) $O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$

(3) $\text{R-CH=CH}_2 + H_2O \rightarrow \text{R-HC}\overset{\diagup O \diagdown}{—}\text{CH}_2 + 2\,H^+ + 2\,e^-$

Scheme 7. Electrochemical reduction of oxygen (1) and epoxidation of alkenes (2)

The understanding of the details of the mechanism of reaction (1) is quite advanced. The Gibbs energy change for these three reactions is similar and hence, energy and a chemical would be co-generated if the reaction could be carried out sufficiently fast in a fuel cell.

8.2 Summarised project objectives

The main specific objectives of the project are:

- Development of a theoretical and computational chemistry to investigate the pathway of the reactions of interest to provide guidelines for the design of nanoscale electrocatalytic materials.
- The synthesis and study of the reactivity of electrocatalytic materials for producing hydrogen peroxide and epoxides in a fuel cell using nanoparticles of different materials as well as the use of redox-catalytic cycles.
- To understand the relationship between crystal orientation of nanocrystalline materials and their electrochemical reactivity.
- Synthesis of novel anionic exchange materials for use in fuel cells.
- Development, modelling and testing a small fuel cell for co-generation of chemicals and energy.

8.3 Contractors involved

1. Helsinki University of Technology (HUT*),* Professor K. Kontturi,
2. Göteborg University (UGOT), Professor E. Ahlberg
3. University of Liverpool (ULIV), Professor D. J. Schiffrin,
4. Johnson Matthey plc (JMTC), Dr. R. Potter
5. Tartu University (UT), Dr. K. Tammeveski
6. University of Alicante (UALI), Professor J. Feliu
7. Heyrovský Institute of Physical Chemistry (HIPC), Professor Z. Samec
8. Technical University of Eindhoven (TUE), Dr. M. Koper
9. University of Ulm (ULM), Professor W. Schmickler

8.4 Co-ordinator contact details

Co-ordinator: Professor K. Kontturi
Organisation**:** Helsinki University of Technology
E-mail: kyosti.kontturi@tkk.fi
Fax No.: +358-9-4512580
Project website: http://www.tkk.fi/Units/PhysicalChemistry/research/NENA%20homepage.html

8.5 Work performed

The strategy followed for the development of the concept of cogeneration of energy and chemicals required the confluence of three strands of activity: experimental selection of electrocatalytic materials, theoretical investigations of reaction mechanisms and construction and testing of fuel cells and appropriate product collection hardware.

8.5.1 Hydrogen peroxide production

Since the aim of the project is to produce chemicals in a fuel cell, the membranes to be used, either acid of basic, play a major role in defining the electrocatalytic materials to be employed. In all cases, a hydrogen anode has been considered and the question that the research had to answer was which cathode to use.

To better understand the important hydrogen oxidation reaction a theory for the electrocatalysis of bond-breaking electron transfer has been developed and a mechanism by which a d-band centered near the Ferrmi level of the electrode can lower the energy of activation for the reaction is proposed. This theory has been tested on a particularly important reaction: the oxidation of hydrogen according to the scheme: $A_2 \rightarrow 2\ H^+ + 2\ e^-$. Potential energy surfaces for the hydrogen oxidation have been calculated, and from these the energy of activation is obtained. At present, variation of the activation energy with the nature of the metal can be calculated. Figure 1 shows a comparison between experimental values for the exchange current density of the hydrogen oxidation and activation energies calculated. There is a good correlation between the calculated values and experiment. In particular, the model explains, why the platinum group metals are such good catalysts: They have both a high density of states near the Fermi level, and high coupling constants. In contrast, the transition metals nickel and cobalt are bad catalysts in spite of their favourable density of states, because their coupling constants are smaller by a factor of three to four.

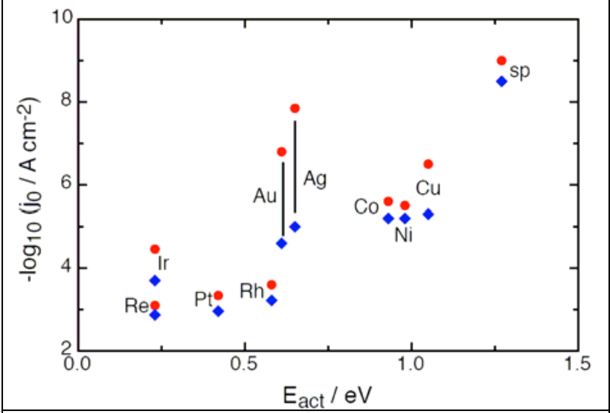


Figure 1. Experimental data for the exchange current density of the hydrogen oxidation versus calculated values for the activation energy. For the sp-metals, values for Cd and Pb have been taken.

A detailed quantum chemical investigation for anthra- and phenanthrenequinone which have been proved to be good catalyst for hydrogen peroxide formation in alkaline media, have been addressed to understand rate determining steps of oxygen reduction reaction on quinones. The aim of this work is to investigate the reaction pathway from oxygen to hydrogen peroxide when the active site is the semiquinone radical. The dependence of reactivity with pH is of fundamental importance in practical fuel cell equipment for cogeneration of energy and chemicals due to the need to define the type of membranes to be employed. It has been found that the reaction of oxygen with protonated semiquinones has a much higher activation barrier than that of the radical anion and quantum chemistry has been successfully used to explain the experimentally observed decrease in electrocatalytic activity in acid media for grafted quinones.

Above mentioned theory is based on the kinetics of O_2 reduction which has been studied on anthraquinone and phenanthrenequinone modified GC electrodes at different pHs (pH=0.3−14). On the basis of these results it may be conclude that the highest electrocatalytic activity of these electrodes is observed in the solutions of high pH (pH>10) and therefore, these catalysts are good candidates for the production of peroxide only in alkaline media. In addition, the spontaneous attachment of quinones has also been studied and this appears to be a suitable method for surface grafting.

Milestone M1 is completed and it can be concluded that the quantum chemical calculations have made a breakthrough in the molecular understanding of the reaction mechanism for oxygen reduction.

Extensive density functional theory calculations on the interaction of oxygen and different intermediates during oxygen reduction on Au surface have lead to a general mechanism for oxygen reduction which gives insight into the nature of the selectivity of the overall reaction, i.e. whether the reaction leads to water or hydrogen peroxide as the final product. These calculations have provided strong evidence that in the presence of water, O_2 adsorbs onto the Au surface as HO_2. This HO_2 acts as a precursor for both H_2O_2 and H_2O formation. If the HO_2 is strongly adsorbed on the surface, water is the main product of the overall reduction. If the HO_2 is more weakly adsorbed, it may desorb from the surface as a HO_2^- (alkaline media) or a H_2O_2 species (acidic media). Therefore the key to forming hydrogen peroxide is to facilitate proton/electron transfer to the oxygen molecule, but to have a weak interaction of the catalyst with the key intermediate, HO_2.

In addition, the mechanism of oxygen reduction on hydroxide clusters has been investigated by quantum chemical calculations. A redox catalytic cycle is proposed for the formation of hydrogen peroxide using metal hydroxide clusters as a model for the active site. This redox cycle is applicable for several transition metal hydroxide and the fact that different amounts of hydrogen peroxide is formed depending on the nature of the hydroxide has been rationalised and prediction of the activity can be made, which has also been shown experimentally. The reduction of O_2 on a model step edge of CoOOH has also been considered in order to determine how constraints of embedding the active site may influence the overall catalytic mechanism. It is shown that the constrain influences the spin structure of the reduced surface site, i.e Co(II) remains in the low spin configuration imposed by Co(III). This creates a surface site for binding of oxygen and formation of hydrogen peroxide.

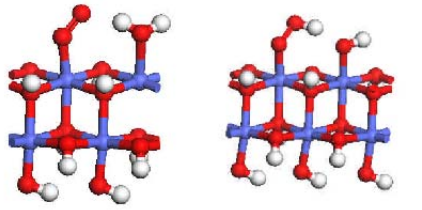


Figure 2. Surface superoxide replacing one water molecule thus producing one Co(III) site in conjunction with a spectator adsorbed water molecule (left) and hydrogen transfer from H_2O to O_2^- producing a surface HO_2^- anion and a hydroxide adsorbed at two Co(III) atop sites (right).

Also a general model for the reduction of oxygen on oxide or hydroxide covered metals has been developed taking into account the conductivity of the solid phase as well as the site specific reduction of oxygen. To elucidate the mechanism of oxygen reduction, a long range of experiments have been made investigating the effect of composition and morphology of the pulse plated layer as well as the effect of pH, electrolyte cations and temperatures. In this context also the decomposition of hydrogen peroxide has been investigated. Both nickel and mixed nickel/zinc hydroxide has been shown to be efficient electrocatalysts for oxygen reduction and the amount of hydrogen peroxide formed ranged from 60–90% depending on the actual parameters. The combined experimental and theoretical approach has resulted in a better understanding of the mechanism and how the activity can be changed to optimise the production of hydrogen peroxide. Delivery reports D2 and D10 have been completed.

Experimentally the oxygen reduction reaction (ORR) has been studied for stepped single crystal platinum surfaces in order to identify both mechanism and products formed (D23), Figure 3. It is observed that the ORR on platinum yields water as the only product, with the exception of the potential region where hydrogen is adsorbed on the electrode surface. The catalytic activity for the reaction increases with the step density. Additionally, the presence of strong anion adsorption diminishes the activity of the electrodes towards ORR. Modified platinum electrodes with sulphur and selenium adatoms (D5) exhibit a better selectivity towards the mechanism producing hydrogen peroxide. Specifically, for S/Pt(hkl), hydrogen peroxide is the only product formed, whereas a narrow potential region for the formation of water is observed for Se/Pt(hkl) electrodes.

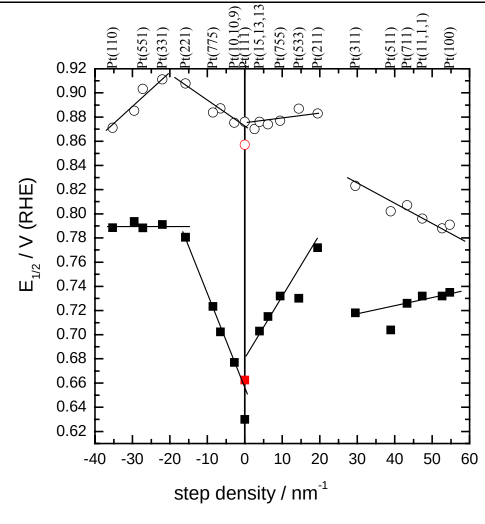


Figure 3. $E_{1/2}$ for ORR in 0.5M H_2SO_4 (■) and in 0.1M $HClO_4$ (○) for different Pt(hkl) surfaces.

A model catalyst approach has been followed in order to establish basic relationships between structure and activity of the electrodes towards ORR. The results indicate that the mechanism of ORR is basically the same for thin-film and bulk Pt electrodes. Measurements with thin Au films have shown that ORR on gold films in acidic media yields H_2O_2, which reduces further only at high negative potentials. There has not been essential change in the specific activity for ORR over the entire range of film thickness (and Au particle size) studied.

The electrochemical reduction of oxygen has also been studied on gold nanoparticle/multi-walled carbon nanotubes modified glassy carbon electrodes and these modified electrodes showed a high electrocatalytic activity for O_2 reduction. The reduction of oxygen stops at the hydrogen peroxide stage on these electrodes in acidic solution. Multi-walled carbon nanotubes (MWCNTs) could be applied as electrocatalysts and catalyse a two-electron reduction of O_2 at low overpotentials in alkaline solution. However, the formed hydrogen peroxide is further reduced at more negative potentials.

Due to the excellent properties and processability of commercially available cation exchange membranes, acid media electrocatalysts have been investigated. The use of transition metal compounds dispersed on carbon has shown high yields of peroxide in strongly acid media, both in measurements at a rotating disk electrode and when this material is incorporated within a fuel cell.

The concept of operating cathodes with mesoscopic ion-exchange properties has been evaluated. The surface of the high-surface area carbon support has been functionalized with hydroxyl-transporting groups such as R_4N^+. Gamma and e-beam radiation as well as chemical grafting of R_4N^+ groups onto carbon has been tried, but the experiments have been unsuccessful. The principal technical hurdle to progress is the poor performance of existing anion-exchange materials and inability to create adequate hydroxyl-ion activity within the local environment of the catalyst surface.

Novel method to synthesize anion exchange layer to a bipolar membrane have been tried but resulted in membranes with poor mechanical properties and low conductivity. However, three promising method have been found: i) grafting of covalently bound cationic grafts on one sides of the Nafion® membrane, ii) amination of hydrophobic membrane with trimethylamin, and iii) irradiation grafting of [3-(methacryloylamino)propyl] trimethyl- ammonium chloride into polyamide matrix (D6, D14).

A series of membrane electrode assemblies (MEAs) have been fabricated and continuously modified to improve the catalyst utilisation and cell performance. One particular catalyst/electrode configuration achieved a current density in excess of 500mA/cm^2 on oxygen at 30psig. In common with MEA development for power applications, the water management properties of the MEA were found to be very important in controlling peroxide yields.

A 50cm^2 single cell test station has been constructed and used to map out the space-time yield characteristics of peroxide generation in fuel-cell mode. The yield of the peroxide production process hs been lifted up to new levels such that the single-cell can produce 8% concentration. It is believed that this figure can be improved further by a combination of development work on catalyst, electrode and cell design. The upper limit of peroxide concentration will be set in part by the humidification regime imposed upon the cell. It is concluded that with this technology, production of peroxide could reach levels of >20%. At such a level, it would be feasible to consider the use of fuel-cell like technology for commercial bulk peroxide production as well as end-user applications.

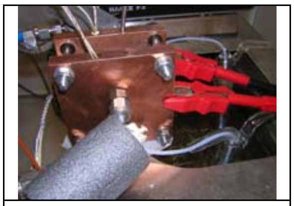


Figure 4. A single-cell fuel cell test unit.

8.5.2 Electrocatalysis of epoxidation reaction

The aim of this work is to develop electrocatalytic materials appropriate for oxygen insertion reactions to double bonds. Oxides and metals have been investigated as electrocatalysts. As described above for the synthesis of hydrogen peroxide, the experimental work has been carried out with the aid of theoretical calculations of reactivity and of the potential energy curves calculated for different reactant and product conformations. The understanding of these reactions is, at present, rather limited. In addition, for oxides, the interfacial potential distribution determining the rate of electrode reactions needs to be understood. Considering these limitations of the state of the art, the research programme developed investigated fundamental aspects of reactivity at metal oxides, single crystal and bulk platinum and gold electrodes, and addressed theoretical aspects of the electronic structure of reaction intermediates and ionic distribution at the oxide-solution interface.

Charging of nano-sized particles is important for surface reactivity in electrocatalytic processes. The surface and interfacial properties of metal oxide particles has been studied in the context of Corrected Debye-Hückel theory of surface complexation (CDH-SC). In this context the theoretical developments continued with 1) development of a new direct method in the context of CDH theory of electrolytes (in this new approach the electrostatic contribution to the chemical potential of electrolyte solutions is obtained directly by minimizing a free energy density functional) and 2) complementing CDH-SC calculations on oxide colloids with Monte Carlo simulations. Well defined nano-sized TiO_2 particles in the range 7–27 nm have been synthesised and characterised. Determination of surface charge and interfacial properties such as zeta potential of nano-sized particles is afflicted with problems due to severe aggregation of the particles (D16).

The partial ethene oxidation has been investigated systematically (M2) and quantum chemical calculations to predict the mechanism on noble metal clusters have been carried out (D4). The modelling of the possible reaction pathways found the ethene oxidation to epoxide to be possible on both major noble metals – Au and Pt. The reactivity of the electrode material depends on its spin state and on the surface morphology. A flat surface seems to be preferential for ethene oxidation of over the edges. The activation energy for the transition state formation is higher for Pt than for Au. Actual yield of epoxide may be, however, low due to competitive reaction pathways leading to formation of carbonyle compounds or carbon dioxide.

The actual electrocatalytic activity of the nano-crystalline and nano-structured noble metals towards ethene oxidation in acid media has been followed by electrochemical and differential electrochemical mass spectrometry (DEMS) techniques. The results confirm the theoretical prediction of higher activity of Au towards ethene oxidation. In both cases the oxidation process proceeds on oxide free surface. Detectable reaction products have been acetaldehyde in the case of Au electrodes and CO_2 in the case of Pt. The morphology of the substrate has a minor effect on the mechanism. All studied noble metals form soluble complexes with ethene which results in gradual dissolution of the electrode which is of chemical nature and in fact restricts the stability of nano-crystalline and nano-structured electrocatalysts. Alloying of these metals leads to formation of bi-functional electrocatalysts. The overall activity is comparable to that of the polycrystalline Au, while the reaction products are the same as in the case of Pt.

Alkene oxidation has also been studied on single crystal electrodes (D32) and according to these experiments only active platinum surface for partial oxidation is Pt(111). No formation of epoxide has been detected in the whole potential range (M4). Carbon dioxide and adsorbed carbon monoxide have been the only oxygen containing species observed. The only ethylene-derived species found by FTIR have been vinylidene species, which appear as intermediates in the partial oxidation of ethene on Pt(111) (M12), see Figure 5.

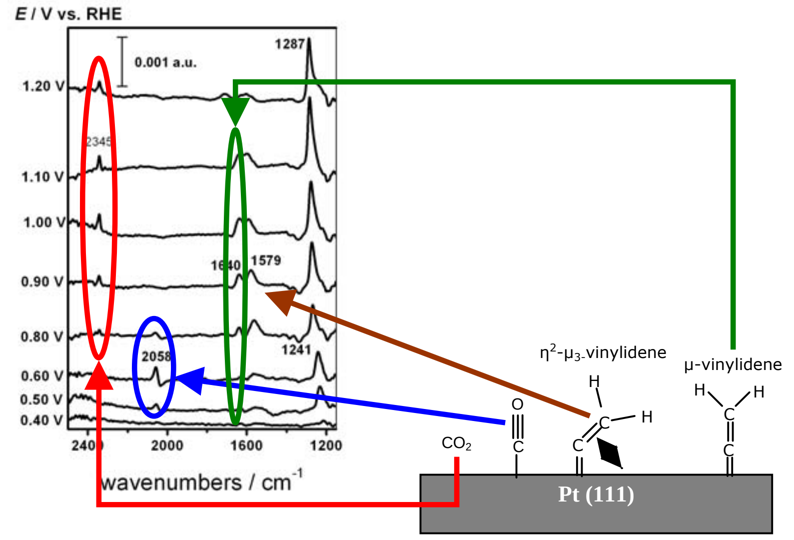


Figure 5. Potential dependent infrared spectra obtained during the adsorption and oxidation of ethene on Pt(111).

Despite the promising results previously reported in the literature, it has been clearly shown that the epoxidation reaction can not be used as an anode reaction in a fuel cell device. However, all the experimental and theoretical efforts made within the project to investigate the reactivity and mechanism of the epoxidation reaction on different materials has shown that the indirect way of epoxide formation may be feasible. By utilising the work made within the NENA project on electrocatalytic hydrogen peroxide formation an electrochemical reactor can be envisaged where *in-situ* formation of hydrogen peroxide is used for the epoxidation reaction (see below).

A positive side effect has been discovered for the electrochemical oxidation of allyl alcohol on both Ni and NiZn in alkaline solution. The oxidation results in the formation of acrolein as the only product, which shows a new effective route for aldehyde formation. The inability of oxidising the double bond has further been proved by investigating the oxidation of propene. No additional electrochemical activity has been observed on Ni and NiZn in the presence of propene.

Because of the problems encountered with the direct epoxidation, indirect hydrogen peroxide and halide ions assisted epoxidation reactions has been investigated in theory and in practice, respectively. In the former, a new mechanism for hydrogen peroxide assisted epoxidation has been formulated, where the stabilization of the transitions state is emphasised. By micro-solvating with water the activation energy is lowered showing that the hydrogen bonded network can act as a catalytic site for the reaction. The mechanism developed applies also to the reaction on hydroxylated metal sites and it has been shown that stabilisation of the transition state by the surface hydroxide groups lowers the activation barrier even further. The mechanism of heterolytic ring opening for ethene oxide under micro-solvation conditions in acidic, neutral and alkaline environments has also been studied. In acid and alkaline media, the mechanism is a concerted *trans* S_N2 reaction, while a high energy pathway prevails under neutral conditions. The crucial role of the nucleophile in both acidic and alkaline media puts constraints on any successful strategy to produce epoxides in aqueous media. However, the stability of the epoxide under neutral conditions is inspiring and can be utilized in the development of epoxidation catalysts (D4).

The ethene oxidation has been directed to ethene oxide only in the case of Ru based oxide electrodes in presence of halide ions. The reaction mechanism seems to proceed via halohydrine pathway reported previously. In contrast to common perception of the process the epoxide formation proceeds even in acid media and the efficiency of the halohydrine to epoxide conversion is affected by the nature of the electrode surface. The highest selectivity towards epoxide formation has been found for the electrocatalysts with high activity to oxygen evolution. Actual reaction mechanism, however, cannot be extracted without use of surface sensitive spectroscopic techniques. The practical potential of these electrocatalysts is yet to be determined with respect to compatibility of the needed reaction system towards proposed fuel cell based technology.

The nanocrystalline Ru based oxides have been developed to control the activity and selectivity of the surface towards halogen and oxygen transfer in the halohydrine forming reaction (D13). The selectivity and reactivity of the surface is controlled by the particle shape and particle surface composition. The presence of large number of edges separating the crystal faces with {110} and {100} orientation is essential to achieve high activity in oxygen transfer reaction. An increase of the oxidation state of ruthenium results in enhanced selectivity towards halogen evolution which in turn deteriorates the epoxide formation efficiency.

8.6 Summary of achievements

1. Catalyst selection for H_2O_2 production has resulted in two materials that can be used in an acid and a basic cathode environment.
2. Fuel cells operating with electrocatalysts developed during the project are giving high yields of peroxide.
3. Quantum chemical calculations have provided important guidelines for catalysts selection
4. A new theoretical approach for analysing the class of reactions investigated, electron and proton transfer, has been developed.

9 Intentions for use and impact

The work on hydrogen peroxide generation has advanced to the point where the industrial implementation of the technique can be foreseen within the next 3-5 years. The industrial partner, Johnson Matthey, has the intention to try to exploit the new methods resulting from the NENA project. The intention in the short term is the installation of the new technology for demonstration purposes. In addition, resulting form several publications by the partners, firms have contacted the groups at the Helsinki University of Technology and the University of Liverpool to enquire about possible acquisition of production modules. Thus, the work carried out has received attention in industry through publications.

The work has also had an impact in the scientific community by establishing a new focus on electrocatalysis and by fostering the relationship between quantum chemical methods applied to analyse important practical problems, and experimental techniques. In addition, theoretical developments underpinning fundamental physicochemical problems in electrosynthesis e.g., the theory of coupled electron and proton transfer reactions, is of importance in many reactions of practical importance.

10 Dissemination

The Dissemination of Information Plan relies on publications in the scientific literature and presentations to meetings. The work of the partnership has already resulted in several publications, with papers either submitted or in preparation. Dissemination of the results of the research within the industrial environment will be actively pursued by the industrial partner after the current testing programme for the first demonstration module is ready for display, and by the Helsinki University of Technology to demonstrate to local industry the potential of the method developed.