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Divulgação

ELECTROCATALYSIS AND ELECTROCATALYSTS FOR LOW TEMPERATURE FUEL CELLS: FUNDAMENTALS, STATE OF THE ART, RESEARCH AND DEVELOPMENT

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This article deals with electrocatalysis and electrocatalysts for low temperature fuel cells and also with established means and methods in electrocatalyst research, development and characterization. The intention is to inform about the fundamentals, state of the art, research and development of noble metal electrocatalysts for fuel cells operating at low temperatures.

Keywords: electrocatalysis; electrocatalysts; fuel cell.

INTRODUCTION

The idea of electrochemical electricity generation from chemical energy in fuel cells originated already more the 150 years ago from the experiments of Grove and Schönbein[1]. However, the technical realisation had to wait for more than a hundred years as the relevant materials problems could not be solved for a very long time and the theoretical background of electrochemistry, not to speak of electrocatalysis, took so much time to be developed. It was apparent from the very beginning that the electrochemical combustion of any fuel (Equation 1) in an electrochemical cell brought about by separate anodic oxidation of a gaseous fuel, for instance hydrogen (Equation 1a), at the anode and cathodic reduction of oxygen (Equation 1b) needed the catalytic activation of the reactants, fuel as well as oxygen.

$$\text{Total reaction: fuel} + (x + y/_{2})\ O_2 \rightarrow x\ CO_2 + y\ H_2O \qquad (1)$$
$$\text{Anodic reaction: } H_2 + 2\ H_2O \rightarrow 2\ H_3O^+ + 2\ e^- \qquad (1a)$$
$$\text{Cathodic reaction: } ½\ O_2 + 2\ H_3O^+ + 2\ e^- \rightarrow 3\ H_2O \qquad (1b)$$

Hydrogen (H_2) is a relatively stable molecule – and so are carbonaceous fuels. Due to the strength of the H-H bond or H_2-binding energy respectively of approximately 430 kJ/mol[2,3], only catalytic activation of this molecule would enhance its reaction at ambient temperature to a degree, which allows it to react with sizeable rate. For double-bonded and hence more strongly bonded oxygen ($\Delta H \cong 500$ kJ/mol) the catalytic activation is even more necessary. This statement holds for gas phase reactions (Equation 1) as well as for electrochemical conversion at electrode surfaces (Equation 1a and 1b). And as will be explained below, platinum in both cases is the catalyst of choice as already realized in the 19th century by Döbereiner[4]. Although this article deals almost exclusively with electrocatalysis in fuel cells, it is stressed that electrocatalysis is of high practical relevance in industrial electrochemistry. The present technology of chloroalkali electrolysis today depends essentially on electrocatalysis of the hydrogen and chlorine evolution reactions[5,6]. In the mid 80ties of the last century the phosphoric acid fuel cell technology gained shape. As documented by a number of important patents of that time it became evident that platinum and also a number of platinum alloys can be prepared on industrial scale in well-defined nanodisperse form, thus enabling fuel cell producing industries to make highest possible use of this expensive material[7-10]. In the same context also the use of active carbon supported nanodisperse platinum had been introduced into the practice of technical production of fuel cells[11].

The developments of modern fuel cells began with moderately high temperature alkaline cells[12] in the 20ies (working at 200 °C) and with high temperature molten carbonate cells[13] in the 50ties of the last century. A first technical application was the development of the alkaline cells for the Gemini space mission by United Technologies Corporation (UTC)[13,14]. The Varta-Siemens approach based on Raney-nickel electrodes in 30 wt% KOH did not lead to a convincing success[14]. Much more promising was the next step undertaken by UTC to introduce membrane fuel cells, which after disappointing experimentations with classical ion exchange membranes led to a technical brake through by introducing perfluorinated sulfonic acid membranes as so-called solid polymer electrolyte[15,16], which had been perfected by Siemens for powering submarines during the last years. Dupont initially had developed this type of membrane under the name of Nafion for the chloroalkali industry[17]. This eventually yielded into the now well-established polymer electrolyte membrane fuel cell (PEMFC) technology (Figure 1). The scanning electron microscopic cut through a so-called membrane/electrode assembly (MEA) of a PEMFC (Figure 2) shows the minute dimensions of only approximately 10 µm thick porous electrodes on both sides of the approximately 150 µm thick membrane. The membrane chemical composition is shown in Figure 3. The essential catalyst for hydrogen/oxygen fuel cells on the anode- and the cathode side is nano-dispersed platinum, supported on active carbon. Its preparation and morphology will be described below.

The further advance of PEMFC-electrocatalyst development was due to the fact that for mobile or for stationary electricity generation with PEMFC using hydrogen, purified hydrogen in particular, seemed to be too expensive and therefore impractical. The relatively reactive and easily processable methanol but also natural gas, which demands higher processing efforts, are cheaper than hydrogen. Methanol additionally because it is a liquid at ambient temperature and pressure is easy to store and more appropriate as fuel for cars whereas natural gas is the primary fuel of choice for

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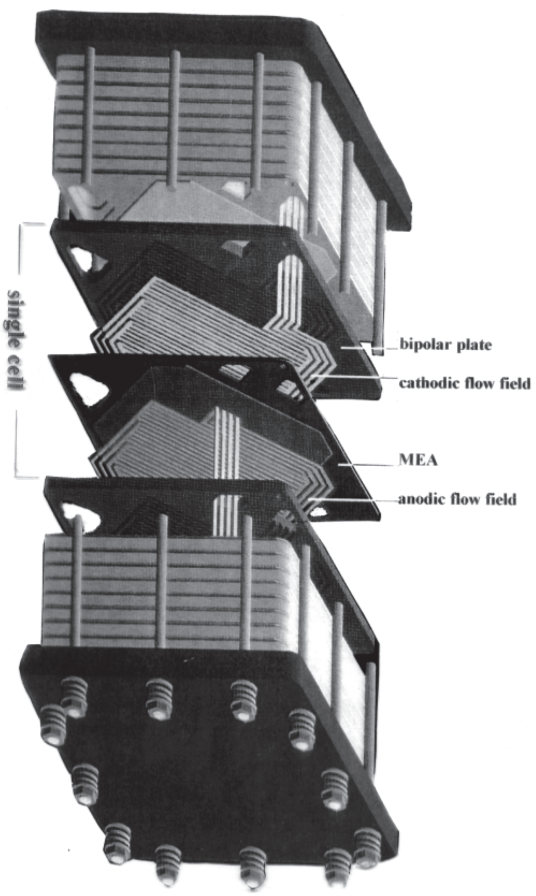


***Figure 1**. View of Proton Exchange Membrane Fuel Cell stack; included is the exploded view of a singular cell containing bipolar wall with flow field and at the centre the MEA (Membrane-Electrode-Assembly)*

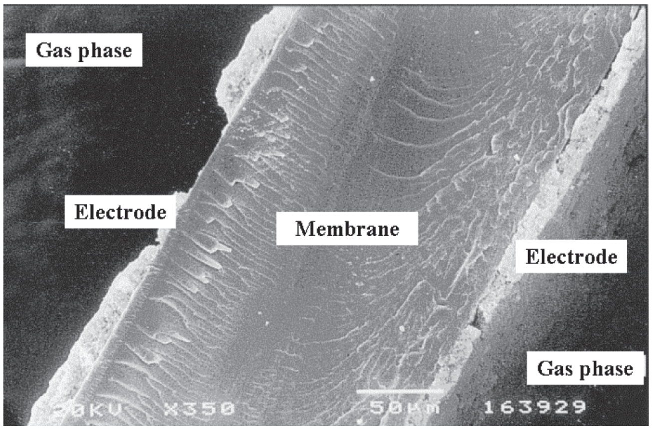
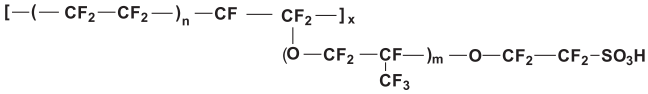


***Figure 2**. SEM micrograph of a typical MEA produced in the laboratory of the authors*



$$\begin{array}{l} [-(-CF_2-CF_2-)_n-CF-CF_2-]_x \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad (O-CF_2-\underset{CF_3}{CF}-)_m-O-CF_2-CF_2-SO_3H \end{array}$$

n = 5 to 13
x = ca. 1000
m = 1 to 3

***Figure 3**. Schematic presentation of the chemical structure of Nafion*

stationary electricity generation. These hydrogen carriers can be converted to hydrogen by the sequence of reforming and shift-conversion (Equations. 2 and 3) that produces gas mixtures containing hydrogen and carbon dioxide but also the catalyst poison carbon monoxide. The latter is found in concentrations of up to one percent because shift conversion is an equilibrium reaction, which favours CO at higher temperature and the equilibrium concentration of CO in reformate gas is that high at the operation temperature of the heterogeneously catalysed shift conversion process (200 °C).

Reformate from methane

Methane reforming:
$CH_4 + H_2O \rightarrow CO + 3H_2$ (800-900 °C) (2a)
Shift conversion:
$CO + H_2O \rightarrow CO_2 + H_2$ (beginning at 400 and ending at 200 °C) (2b)

Reformate from methanol

Methanol cracking and reforming:
$CH_3OH \rightarrow CO + 2\ H_2$ (300-400 °C) (3a)
Shift conversion:
$CO + H_2O \rightarrow CO_2 + H_2$ (beginning at 400 and ending at 200 °C) (3b)

The generation of hydrogen from carbonaceous hydrogen carriers therefore is highly problematic with respect to the CO – sensitive platinum catalysts if the electrochemical reaction is to be performed at temperatures of between 60 and 80 °C, which is the case in PEMFCs. Their working temperature must be kept that low because of the necessary moisture in the membrane, which keeps the ionic conductivity of the membrane sufficiently high. At these low temperatures the catalytic activity of platinum is severely impaired by strongly adsorbed CO, as long as the CO concentration is not kept lower than only 10 ppm. Direct methanol fuel cells (DMFCs)[18] for automotive power generation and for so-called portables applications are even more demanding with respect to the anodic electrocatalysts. There the electrocatalyst has not only to provide for the anodic fission of O-H and C-H bonds by chemisorption of the respective fuel but the anodic oxidation of methanol ends up generating adsorbed CO in situ and thus the reaction on Pt is poisoning the catalyst. And this catalyst poison has to be removed steadily. Therefore, during the last years a couple of cocatalysts has been investigated and applied which enhance particularly the oxidation rate of CO in order to render anodic PEM-electrocatalysts more CO-tolerant. Among these cocatalysts ruthenium is the most prominent. It is technically applied since several years and it is very well documented and investigated[19]. Binary Pt/Ru catalysts supported on active carbon are commercial products. This article will therefore deal not only with dispersed platinum electrocatalysts, their preparation and characterization but will report briefly also on what we know today about composition, structure and nanomorphology of more elaborate nanodisperse, composite electrocatalyst systems. These more involved anodic catalyst systems, as far as they are used in PEMFCs, are almost exclusively supported on active carbon[20-22].

Phosphorous acid fuel cells (PAFCs) working at 200 °C are insensitive against CO and work on reformate with 1% of CO (without CO removal). But according to an announcement of UTC in 2003 (source: Internet, Hyweb) they will develop PEM fuel cells in preference to PAFCs for stationary electricity generation because the PAFC – technology does not promise any further cost reduction below the established system costs of 4,500 USD per kW.

FUNDAMENTALS: PLATINUM, THE CATALYST OF CHOICE FOR ANODIC HYDROGEN OXIDATION AND CATHODIC OXYGEN REDUCTION

Exchange current densities, an indicator of electrocatalysis

Current voltage correlations measured for the Butler-Volmer equation (Equation 4), describe mathematically the current-voltage correlation for a reversible electrochemical reaction, for instance, the anodic oxidation of hydrogen and cathodic hydrogen evolution. It comprises an anodic (*index a*) and a cathodic (*index c*) exponential terms with the overpotential η being the difference between actual electrode potential E and equilibrium potential E_o ($\eta = E - E_o$) and the charge transfer coefficients α_a and α_c in the exponent. Instead of current, I, the current density (current per unit surface), i, is chosen as the adequate quantity for this correlation, in order to obtain an equation, which is independent of the size of the electrode.

$$i = i_o (\exp \{\alpha_a F\eta / RT\} - \exp -\{ \alpha_c F\eta / RT\}) \qquad (4)$$

In the Butler-Volmer equation the exchange current density, i_o, as the quantity describing charge exchange per unit surface at equilibrium potential in cathodic and anodic direction, is an indicator for electrocatalysis. Table 1 collects the well-established charge exchange current densities observed at different electrode materials whose numerical values range from 10^{-3} down to 5×10^{-13} Ampere per square centimetre (A cm^{-2}) over more than twelve orders of magnitude. Obviously the metals contained in the group of the platinum metals (Pd, Pt, Rh, Ir and, not reported here, also Ru) at which the hydrogen reaction is recorded to have the highest exchange current densities, do catalyse this reaction. They are good electrocatalysts for this reaction, whereas mercury on which an exceedingly low exchange current density is reported is not an electrocatalyst at all[6].

Cyclic voltammetry at smooth platinum, an indicator of H-electrosorption and electrocatalytic activity for hydrogen evolution

The cyclic voltammogram of a platinum electrode immersed in acid electrolyte is depicted by broken line in Figure 4, which would be very similar in any electrolyte of any pH, provided that electrosorption of components of the electrolyte on platinum can safely be excluded[23]. One observes a relatively flat anodic and a very steep cathodic current increase at the right and left hand side of the plot, which are due to anodic oxygen and cathodic hydrogen evolution. The peaks and waves between electrochemical gas evolutions are due to electrochemical surface reactions at the platinum electrode. The voltammogram is observed by sweeping continuously the electrode potential with constant velocity of, for instance, 10 mV per second and thereby measuring the electrode current. Positive current peaks or waves do mean anodic oxidation processes and negative currents are correspondingly due to cathodic reactions at the platinum/electrolyte interface. A constant current between 0.3 and 0.6 V signify charging of the electrode/electrolyte interface, which forms a capacitance. The electrode potential is measured with reference to the Reversible Hydrogen Electrode (RHE) in the applied electrolyte. Beginning at 0 V vs. RHE, where the observed current is zero, one observes two oxidation peaks one centred around +150 and the other around +300 mV, which are attributed to the anodic oxidation of adsorbed hydrogen ($H_{ad}^{I, II} \rightarrow H^+ + e^-$), which due to the respective different adsorption sites are adsorbed with different strengths. At 150 mV the free energy of adsorption corresponds to –14.5 kJ/mol and correspondingly the second peak signifies a free adsorption enthalpy of approximately –29 kJ per mol of adsorbed hydrogen atoms (reaction: $½H_2 \rightarrow H_{ad}$). These weak free adsorption enthalpies evidence that the binding energy of two H-atoms on platinum almost matches the dissociation/binding energy of the H-H bond. Neglecting for the moment the further anodic details of the voltammogram at more anodic potentials one observes on reversal of the voltage sweep cathodic currents and electrosorption peaks of hydrogen ($H^+ + e^- \rightarrow H_{ad}$), which mirror the discussed electrodesorption peaks at +300 and +150 mV. This evidences that the electrochemical reaction $H^+ + e^- \rightarrow H_{ad}$ is a fast and reversible reaction on the time scale of the voltage sweep. These cathodic electrosorption and anodic electrodesorption peaks signify the pronounced adsorptive properties of platinum. Similar peaks are also observed at electrodes of other platinum metals, which are known to adsorb hydrogen[23].

Table 1. Exchange current densities of the hydrogen evolution/anodic oxidation reaction at different electrode materials in aqueous 1 N H_2SO_4 solution at ambient temperature

Metal	i_o/A cm^{-2}
Palladium, Pd	1.0×10^{-3}
Platinum, Pt	8.0×10^{-4}
Rhodium, Rh	2.5×10^{-4}
Iridium, Ir	2.0×10^{-4}
Nickel, Ni	7.0×10^{-6}
Gold, Au	4.0×10^{-6}
Tungsten, W	1.3×10^{-6}
Niobium, Nb	1.5×10^{-7}
Titanium, Ti	7.0×10^{-8}
Cadmium, Cd	1.5×10^{-11}
Manganese, Mn	1.3×10^{-11}
Thallium, Tl	1.0×10^{-11}
Lead, Pb	1.0×10^{-12}
Mercury, Hg	0.5×10^{-13}

Proceeding further with the sweep of the electrode potential to more positive potentials one passes through a region, where only a weak and constant anodic current is observed which signify only charging the capacity of the electrode double layer. Then a little bit above 600 mV the anodic current begins to rise approaching a current niveau above 800 mV. This increasing

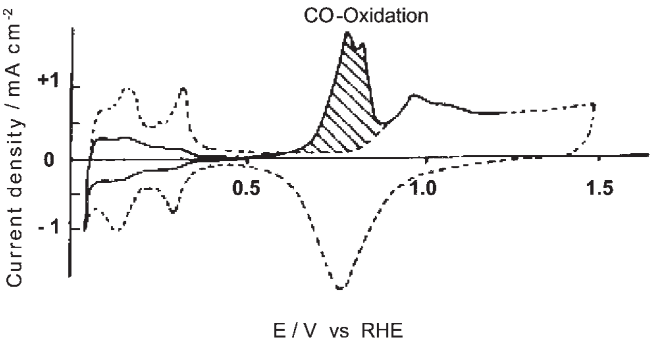


Figure 4*. Cyclic voltammograms of a platinum electrode in acid solution (broken line) and CO-poisoned demonstrating anodic stripping of CO above 0.6V vs. RHE due to oxidation of adsorbed CO by anodically formed Pt-oxide*

anodic current above 600 mV is connected to the beginning of surface oxidation of platinum ($\mathrm{Pt} + \mathrm{H_2O} \rightarrow \mathrm{PtOH}_{\text{surface}} + \mathrm{H^+} + \mathrm{e^-}$), which forms a closed Pt oxide layer at approximately +800 mV. The almost constant anodic current, which is observed further, at still higher potential, serves then only to increase the thickness of the oxide layer and to increase the degree of oxidation of Pt (increasing the formal valency of the metal from +1 to higher values). Above 1.4 V, well above 1.2 V, the equilibrium potential of the oxygen electrode – the anodic current rises again and exponentially with electrode potential due to the onset of anodic oxygen evolution which shows a remarkable anodic overpotential because the reaction $\mathrm{H_2O} \rightarrow \frac{1}{2}\,\mathrm{O_2} + 2\mathrm{H^+} + 2\mathrm{e^-}$ is slow, kinetically hindered and Pt – oxides, which cover the electrode surface, are not particularly active catalysts to enhance it. Reversing the sweep leads to fast decline of anodic oxygen evolution currents and surface oxide charging currents. A broad cathodic current peak shifted negatively with respect to 0.6 V, the onset potential of Pt oxidation demonstrates the retarded reduction of the Pt-oxides. They can only be reduced with some cathodic overpotential because these oxides are (due to aging and further oxidation at higher potential) no longer the same and more stable and chemically more inert than those, which had been formed initially between +600 and +800 mV. Then approaching closer to the hydrogen equilibrium potential (0 V vs. RHE) one observes the cathodic electrosorption peaks for cathodic deposition of adsorbed hydrogen in two different adsorption states, which had been discussed before. Almost exactly at 0 V the cathodic hydrogen evolution current commences to increase steeply and exponentially with increasing overpotential. This increase is much steeper than that of the anodic oxygen evolution. Electrochemical ad- and desorption and electrochemical hydrogen evolution can be slowed appreciably or completely suppressed by strongly adsorbed substances – compare for CO-adsorption in Figure 4. Three items are immediately extracted from this cyclic voltammogram:

i) Hydrogen is relatively strongly adsorbed on platinum and this voltammogram reveals different adsorption states with different adsorption enthalpies – both with a fixed stoichiometry. In contact with aqueous electrolyte at least two different adsorption sites on polycrystalline Pt can be identified with a free adsorption enthalpy of roughly –15 and –30 kJ per mol of adsorbed H. This adsorption is a stoichiometric reaction with Pt: H = 1:1, which allows coulometric determination (Integral [i dt]) of the free surface of Pt of disperded platinum.

ii) At platinum hydrogen evolution, and electroadsorption/electrodesorption are fast, strongly catalysed approximately reversible reactions demanding little, almost negligible overpotential. The assumption of microscopic reversibility for this reaction on Pt/electrolyte interfaces is justified, provided this interface is clean and not blocked by electrosorbed species of any kind.

iii) In contrast, the anodic oxygen evolution does not proceed at the metallic Pt/electrolyte interface because this Pt metal is almost completely covered by Pt oxides already at +800 mV vs. RHE that means already at a potential more negative than 400 mV compared to the oxygen equilibrium potential. On these Pt oxides, the oxygen evolution and reduction is only weakly catalysed and comparatively much slower than cathodic hydrogen evolution on metallic platinum. Since the double bonded oxygen molecule is relatively stable, neither its reductive splitting nor its anodic formation is fast, must be particularly catalysed and cannot be expected to be a microscopically reversible process.

Volcano plots correlating Me-H bond strengths and catalytic activities

An approach to explain the particular role of platinum as an electrocatalyst for anodic hydrogen oxidation and cathodic hydrogen evolution is correlating the catalytic activity of different metals for this reaction and the strength of the adsorption enthalpy of hydrogen on these metals in Figure 5 [6]. In this figure the current densities measured for cathodic release of hydrogen at a given overpotential are plotted vs. the strength of the Me-H bond (calculated in kJ/mol). The reader may be reminded, that free H–adsorption enthalpies for immersed electrodes, as determined from a voltammogram and Me-H bond strength are not identical but related to each other. Figure 5 reveals in the so-called volcano curve a maximum of obtained current densities and hence electrocatalytic activities for intermediate Me-H bond strengths. That means that with lower bond strengths the interaction between adsorbate and metal is too low to allow for an effective activation of the H-H bond whereas with high Me–H bond strengths the adsorbed hydrogen is bonded too strongly to the electrode surface, so that is inactivated with respect to further reaction – be it further anodic oxidation in a fuel cell or reaction to liberated $\mathrm{H_2}$ in cathodic hydrogen evolution. Therefore the Me-H binding energy of two hydrogen atoms approximately matches the binding energy of the $\mathrm{H_2}$-molecule at most of the platinum metal group. It must be underlined that the volcano curve of Figure 5 is by far not restricted to electrochemical hydrogen reactions but is also observed for chemical reactions, for instance, for hydrogenation reactions of different unsaturated organic compounds and therefore is an indication for chemical catalysis of hydrogen splitting rather than for the charge transfer, that is the electrochemical steps.

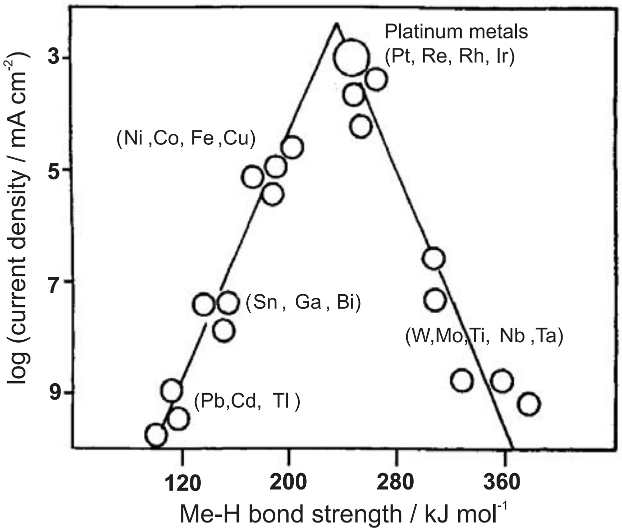


***Figure 5**. Volcano-type correlation of catalytic activity of different metals and the Me-H binding energy*

A different more fundamental approach to electrocatalysis of the anodic hydrogen oxidation consists in modelling hydrogen adsorption by theoretical chemical means, i.e., by calculations based on the functional density theory[24]. This approach aims at estimating binding energies of adsorbed hydrogen by calculating the surface specific number of empty d-electron states or d-orbitals respectively protruding from the metal surface towards the electrolytes (or for gas phase reactions towards the vacuum) at the metal surface. By taking into account the electronic binding energy of these d-orbitals of the metal (Fermi niveau) and the binding energy of electrons, coming from adsorbed molecules the energy of adsorption is calculated. This constitutes the strength of adsorption bonds of different adsorbates and allows calculating the binding energy of different adsorbed species, for instance hydrogen or carbon monoxide. For different platinum metal group and their alloys the results showed that hydrogen and carbon monoxide adsorption follow the same dependence that means, the stronger hydrogen is adsorbed, the stronger is also the adsorption of CO[25].

Electrocatalysis and cocatalysts for CO-oxidation

Carbon monoxide, CO, is strongly adsorbed on platinum and other metals of the platinum group and it is particularly inert against anodic oxidation, although thermodynamically its oxidation potential is calculated at almost the equilibrium potential of hydrogen. Figure 4 shows a typical voltammogram of platinum electrode immersed in aqueous acidic solution that had been exposed to CO and was recorded after thorough purging of the electrolyte with Ar or N_2 or another inert gas, which expels CO from the electrolyte completely. Even after removal of the carbon monoxide from the solution, the platinum surface remains completely blocked by carbon monoxide[26]. This is first of all documented by the absence of the anodic peaks for adsorbed hydrogen, because of complete displacement of adsorbed hydrogen by much more strongly adsorbed carbon monoxide. Additionally one observes at anodic potential of approximately 0.6 V a relatively broad peak (typical for strongly hindered and slow electrochemical processes), which is due to anodic oxidation of the adsorbed carbon monoxide
($CO_{ad} + H_2O \rightarrow CO_2 + 2\,H^+ + 2e^-$). This process is called anodic stripping. And the anodic CO-stripping potential is kinetically – not thermodynamically – controlled proceeding with a high anodic overpotential. It is known, that this retarded oxidation is not a simple electrochemical reaction but that CO-oxidation is mediated by Pt-oxides, which are beginning to form at +0,6 V vs. RHE. Therefore the observed anodic CO-stripping can be formulated in two steps (Equations 5a and 5b):

$$Pt + H_2O \rightarrow PtOH + H^+ + e^- \tag{5a}$$
$$CO_{ad} + 2\,PtOH \rightarrow CO_2 + 2\,Pt + H_2O \tag{5b}$$

The platinum oxide is immediately recuperated by anodic oxidation of the platinum surface at the anodic stripping potential. Only at such high overpotential the platinum surface is cleared of adsorbed CO and only then it becomes available for electrocatalyzed hydrogen oxidation. This means that CO-contaminated hydrogen can only be oxidized at anodic overpotential close to and above 0.6 V. A similar situation does also prevail with anodic oxidation of methanol, ethanol or other energy alcohols, because by their anodic conversion always strongly adsorbed CO is generated which poisons the platinum catalyst after very short time. Therefore metal-additives as cocatalysts are necessary which are more easily oxidized then platinum and whose oxides are able to oxidise adsorbed CO at much lower potential than would platinum oxide.

In Figure 6 is shown the current-voltage curves using an active carbon supported platinum anode for oxidation of pure hydrogen and hydrogen with 150 ppm of CO but using a modified platinum catalyst which contains other metals as a cocatalyst[27]. Clearly the presence of 150 ppm of CO almost destroys the catalytic activity of platinum for anodic hydrogen oxidation due to adsorptive poisoning as almost no current can be drawn from the anode. The addition of other metals, which by themselves are no H_2-oxidizing catalyst, as a potent cocatalyst in a Pt:Me (atomic ratio of 1:1) restores the catalytic activity of platinum. The effect is due to oxygen-transfer or spillover from metal oxides, which are already formed at close to +0.2 V. Interesting enough recent investigations of Baltrushat and co-workers[28] had shown that this effect is produced even if relatively small amounts of molybdenum are adsorbed on platinum.

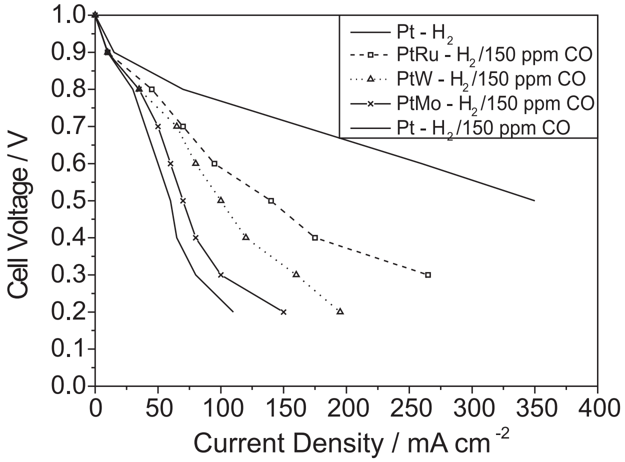


***Figure 6**. Current-cell voltage correlation of PEMFC with pure and CO-contaminated hydrogen for supported pure Pt-electrocatalyst and binary-electrocatalyst (Pt-loading 0.4 mg cm^{-2}, 75 °C, 1 bar)*

The bifunctional electrocatalyst formulation

The first and practically still most important binary catalyst formulation for anodic reformate and methanol conversion is ruthenium which had already been mentioned in the famous conference report edited by Sandstede in 1968[29]. The remarkable cocatalytic efficiency of ruthenium is based on the observation, that this metal is less noble than platinum and oxidizes at a potential at least 0.2 V more negative than platinum and that ruthenium surface oxides/hydroxides therefore can act as a chemical oxidant for CO adsorbed on Pt at a potential, which is between 0.3 and 0.4 V more negative than anodic stripping from pure platinum would demand – provided ruthenium surface oxides and platinum are directly neighboured as would be the case in a surface alloy or if at least Pt and Ru particles would touch each other and the surface diffusivity of CO on platinum is high enough[30], which is the case. Therefore in this case the composite catalyst is called to be "bifunctional", as the platinum due to its adsorptive properties cares for bond breaking in H-H, O-H and C-H groups, whereas ruthenium in the form of its surface oxides mediates the chemical oxidation of the strongly adsorbed poison CO. But ruthenium is not singular and quite a number of elements particularly transition elements like Mo, W and also Ni, all being much less noble than Pt can act as cocatalysts in exactly that sense. The total mechanism is very similar to the anodic stripping reaction of Equation 5, as given by Equations 6a and 6b,

$$Me + H_2O \rightarrow MeOH + H^+ + e^- \tag{6a}$$
$$CO_{\text{adsorbed on Pt}} + 2\,MeOH \rightarrow CO_2 + Me + H_2O \tag{6b}$$

where, Me could be any metal being adsorbed on or alloyed with platinum and which is oxidized at potentials between 0 and 0.6 V vs. RHE as, for instance, Mo, W or others. Table 2 collects some of the alloying elements that had been shown to possess cocatalytic properties in binary Pt-metal electrocatalyst formulations[31]. A particular case is tin. Tin forms a well defined

Table 2. Composition of various CO-tolerant binary Pt-based electrocatalysts

Adittive	Composition
Ru	$Pt_{35}Ru_{65}$
	$Pt_{57}Ru_{43}$
Co	$Pt_{57}Co_{43}$
	$Pt_{82}Co_{18}$
Ni	$Pt_{58}Ni_{52}$
	$Pt_{76}Ni_{24}$
Fe	$Pt_{85}Fe_{15}$
	$Pt_{95}Fe_{0,5}$
Sn	Pt_3Sn
Mo	$Pt_{45}Mo_{55}$
	$Pt_{67}Mo_{33}$

alloy Pt_3Sn, which is an active and particularly efficient cocatalyst for CO-oxidation[32], whose use in membrane fuel cells might become state of the art within the next years.

Anodic oxygen evolution in electrolysis processes and cathodic oxygen reduction in fuel cells

Anodic oxygen evolution in aqueous solutions applied, for instance, in water electrolysis or metal electrowinning processes, Equation 7,

$$H_2O \rightarrow 2H^+ + ½\,O_2 + 2\,e^- \tag{7}$$

proceeds always at metal oxide covered metal electrodes, the anodic overpotential usually exceeding 0.2 V and is supposed to proceed according to the so-called Krasilch'shikov mechanism[6], in which unstable, overoxidized metal oxide sites are self stabilizing by mutual redox- or disproportionation reactions by release of molecular oxygen (schematically described by Equation 7a and 7b) with regeneration of the lower valent metal oxide:

$$Me_xO_y + H_2O \rightarrow Me_xO_yOH + H^+ + e^- \tag{7a}$$
$$4\,Me_xO_yOH \rightarrow 4\,Me_xO_y + O_2 + 2\,H_2O \tag{7b}$$

This mechanistic interpretation is based on the observation, that searching for a volcano-like correlation the correct quantity for correlating different catalytic activities has little to do with adsorption of oxygen. It is simply the free enthalpy of formation of the overoxidized metal oxide sites – namely the free enthalpy of formation of the higher oxide from the stable metal oxide. The maximum, the tip of the volcano, is observed, where the equilibrium potential for the lower valent and higher valent metal oxides (which can be calculated from the Gibbs-enthalpy of the oxidation reaction of the metal oxide) matches that of the equilibrium potential of the oxygen electrode (+1.2 V vs. RHE)[33].

Mechanism of the cathodic oxygen reduction

Because of non-existing microscopic reversibility the cathodic reduction of oxygen follows, however, quite a different route than oxygen evolution. By adsorptive interaction of O_2 with the noble platinum metals the molecule is activated towards bond-splitting and electron uptake. The best electrocatalyst for cathodic oxygen reduction hitherto known is platinum metal. Referring to the cyclic voltammogram of Figure 4, one observes the formation of surface oxides on a platinum electrode above +600 mV and the anodic current reaches a plateau above +800 mV as an indication of the formation of an almost closed platinum oxide layer that grows steadily. But even at +800 mV still a minute fraction of the metal surface is not covered by Pt oxide (PtOH) but it becomes less and less with increasing the electrode potential. The degree of coverage, Θ, in a simplified correlation, follows a type of electrochemical Langmuir isotherm, Equation 8a and 8b

$$\Theta / (1- \Theta) = K_{ox} \tag{8a}$$
$$K_{ox} = \exp\,(E - E_{1/2}\,)\ F / RT \tag{8b}$$

where, Θ is the degree of coverage of the surface by the oxide and K_{ox} is the potential-dependent equilibrium constant. $E_{1/2}$ is the potential at which half of the surface is covered by the oxide. Practically this is the potential at half of the surface oxidation current is measured (approximately 0.7 V). Equation 8a and 8b are only to be understood in a schematic way, but they demonstrate the most important fact, that increasing the anode potential still leaves a smaller and smaller but still finite rest of the platinum surface uncovered by oxide. Therefore oxygen adsorption and reduction is not a question of yes or no but of the degree of Pt-oxide coverage, which depends for a chemical equilibrium reaction on the applied electrode potential.

The adsorptive interaction of electron-donating double bonded oxygen and empty d-orbitals at the Pt-surface acting as acceptors with the ability of d_{Π} - p_{Π}^* back donation activates the oxygen molecule to an extent which allows for a fast transfer of four electrons, a fast sequence of several electron transfer and chemical steps, which are today not yet completely elucidated. This explains, why a relatively high cathodic overpotential of at least – 0.2 V is necessary in order to start with cathodic oxygen reduction at Pt–electrodes, as a rough calculation on the basis of Equatiion 8a clarifies, that the fraction of free metallic surface atoms amounts to roughly 10^{-3} at 1 V vs. RHE (– 0.2 V vs. oxygen equilibrium).

Electrocatalyzed oxygen reduction proceeds at Pt–electrodes only on metal–sites in the adsorbed state and two parallel reaction pathways are observed in acid solution: the direct reduction of O_2 to H_2O (Equation 9a) and an indirect pathway with H_2O_2 (Equation 9b and 9c)[26,34]:

Direct reduction

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^0 = 1.23\ V \tag{9a}$$

Indirect reduction

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E^0 = 0.682\ V \tag{9b}$$
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = 1.77\ V \tag{9c}$$

In order to the oxygen reduction reaction to take place, the oxygen bond must be weakened, which in turn implies that a strong interaction with the surface of the catalyst will be necessary. If the adsorption of the O_2 molecule is end-on, this does not weaken the O-O bond sufficiently, and the indirect mechanism is favoured, whereas bidentate bonding of the O_2 to a surface metal atom, or bridge bonding between two surface metal atoms will favour the direct process, since in this way the O-O bond is substantially weakened[26,34]. The 2-electron reduction of oxygen to hydroperoxide with still intact O-O bond ($O_2 + 2e^- + H_2O \rightarrow H_2O_2$) is produced, for instance, by O_2–reduction to hydroperoxide (H_2O_2) on graphite electrodes in an industrial process in the pulp and paper industry as bleaching agent.

HIGHLY DISPERSE PLATINUM AND PLATINUM ALLOYS: THE ELECTROCATALYST FOR PHOSPHORIC ACID AND MEMBRANE FUEL CELLS

Dispersed platinum invented for phosphoric acid fuel cells

Already in the late 70ies of the last century UTC (United Technology Corporation) developed highly disperse platinum supported on active carbon as anodic (H_2 oxidation) and cathodic (O_2 reduction) electrocatalyst for phosphoric acid fuel cells[10]. Much older had been the use of so-called platinum black as a form of – although not very well defined – disperse platinum metal for catalytic purposes for instance in the Döbereiner lighter (the oldest and very popular application) and for catalytic hydrogenations in synthetic organic chemistry. Already in this very early times of the 18th century existed the idea to increase the effective catalytic activity of the metal catalyst by dispersing the material as finely as possible. The relevant idea was to make highest possible use of the precious metal by dividing it into very small crystallites. Thus the relevant surface to volume ratio according to Equation 10 for a globular particle can be approximated by 3/r, with r being the particle radius. Thus for a particle of 1 nm (10^{-9} m or 10 Å) the surface to volume ratio amounts to 10^7 cm^2/cm^3 = 10^7 cm^{-1}. Even more impressive than this number is the knowledge, that in a globular platinum particle of approximately 2 nm diameter roughly 1/3 of all platinum atoms are exposed to the surface and only 2/3 are buried in the interior of this particle.

$$(\text{Surface/Volume})_{\text{spere}} = 4\Pi r^2 \ / \ 4/3\ \Pi r^3 = 3/r \qquad (10)$$

Practically the utilisation of platinum cannot be expected to be much greater in a particle intended to be stable long term in an operating fuel cell. Highly dispersed materials are thermodynamically unstable. Due to their high surface energy they tend to agglomerate, which would decrease the excess surface energy. Hence fast deactivation of the catalyst due to "sintering" would occur. Anchoring such particles by adsorption on the surface of active carbon allows separating these particles from each other stabilizing them long-term. Figure 7 shows a micrograph of such active carbon-supported platinum-ruthenium nanoparticles obtained by transmission electron microscopy[35]. The carbon supported Pt catalysts prevents the fast agglomeration of the nanoparticles, a process that would occur with platinum black, because the platinum particles are touching each other.

INDUSTRIAL ACTIVE CARBON SUPPORTED ELECTROCATALYSTS, THEIR PROPERTIES AND PREPARATION

Properties of active carbon

Active carbon is a technical mass product, a type of soot, obtained by incomplete combustion and gas phase pyrolysis of hydrocarbons, unsaturated hydrocarbons as ethene (ethylene) and ethyne (acetylene) and aromatic compounds in particular[11]. The production procedure secures reproducible qualities both with respect to specific surface and with respect to surface chemistry. Active carbons come in different qualities and most frequently are amorphous and possess an inner surface of the order of from several tens to several 100 m^2 per gram. Two of the most popular qualities are Black Pearls 2000® with approximately 1.300 m^2 per gram and Vulcan® XC-72 with 250 m^2 per gram both from Cabot Corp. Literally there are hundreds of different active carbon qualities available on the market. The surface of active carbons is to some extent oxidized, carrying hydroxyl-, carbonyl-, carboxylate-, ester-, ether- and quinone-groups and unsaturated groups – sometimes also nitrogen. Upon oxidation by strong oxidants like chromic acid they obtain cation exchange properties[11]. Active carbons are, due to their high inner surface, thermodynamically unstable with respect to bulk graphite but non the less they are so inert, that they resist reductive and oxidative attack and form a material, which is long term stable in low temperature fuel cells even at the cathode side, where the working potential is oxidative (+800 mV vs. RHE). Their practical stability is accounting for life times of 20.000 h (vehicles) or even 40.000 h at 200 °C in phosphoric acid fuel cells. It should be kept in mind, that for instance in phosphoric acid fuel cells on the cathode, half of the supporting active carbon disappears by anodic oxidation within 40.000 h of service time or approximately within four years.

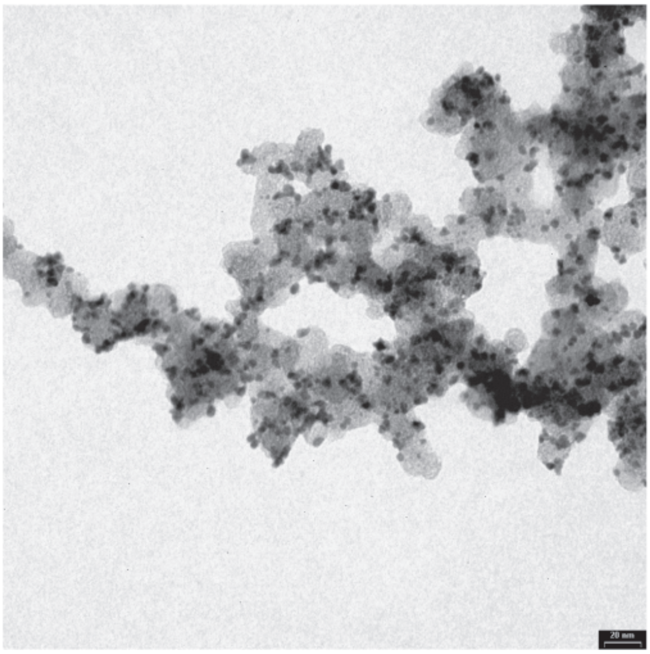


***Figure 7**. Transmission electron micrograph of PtRu/C electrocatalyst (20wt%, Pt:Ru molar ratio 1:1) prepared by alcohol-reduction process*

Preparation of dispersed platinum and active carbon supported platinum

The preparation of highly dispersed metals proceeds according to two principally different lines[36,37]:

1) On one hand the metal can be prepared separately as a sol or stabilized, solvated (not precipitated) nanodisperse material by deposition of the small metal particles from aqueous solutions of respective salts. Most commonly the precipitation is accomplished by strong reductants and assisted by the presence of surface-active substances, which help to prevent growing of the crystals beyond a certain size.

2) On the other hand the dispersed metal particles can be obtained on the active carbon surface after impregnating the material with noble metal salt solutions, slow drying with salt deposition on the active carbon followed by reduction. The reductive treatment may be most commonly performed by dissolved reductants as formaldehyde or hydrazine or may be performed by flowing hydrogen or other gaseous reductants at relatively low temperature (200-300 °C). As a reductant one may also use the supporting active carbon proper at higher temperatures exceeding 400 °C. By this way the so-called cabothermic reduction

of the metal salts on active carbon can be performed.

Concerning these two lines, the preparation of highly dispersed platinum have been done by different approaches[37]:

i) Sols of the metal are obtained for instance by an initial formation of a metastable platinum – sulfito complex, which is inert at ambient temperature but decomposes and produces the small Pt-crystallites at temperatures in excess of 60 °C. Thus a relatively well-defined crystal size of from 2 to 6 nm can be obtained. Bringing then active carbon into contact with the sol "solution" results in anchoring of the metal crystallites on the carbon surface.

ii) Impregnating the active carbon by aqueous or nonaqueous, organic solvents containing platinum salts assisted by the addition of dissolved wetting agents, followed by drying the impregnated material leads to a relatively homogeneous distribution of platinum salts on the active carbon material. Successively reducing these salts, for instance with hydrogen at relatively low temperatures allows creating nanoscale platinum particles whose diameter vary, depending on reduction and preparation conditions, between 2 and 8 nm.

iii) Chemical oxidation of active carbon by strong oxidants as for instance by aqueous solution of chromic acid creates acidic groups (OH-groups, phenolic, and carboxylate groups) on the active carbon surface, which make the active carbon a cation exchange material. From aqueous solutions, which contain positively charged platinum complexes and entities (for instance, amino-complexes of Pt^{+2}), these moieties are absorbed and bound to the active carbon by ion exchange. Chemical or (less often used) electrochemical reduction produces the dispersed metal on active carbon.

Platinum alloys and composite multi-metal catalysts for the anodic oxidation of carbon monoxide containing reformate, of methanol and other energy alcohols

As documented by a considerable number of patents already in the late 70ies the developers of phosphoric acid fuel cells had detected that from highly dispersed platinum on active carbon, dispersed platinum alloys can be obtained by impregnating of the catalyst with aqueous solutions of transition metal salts and subsequent drying and heat treatment[36]. Subsequent leaching of the active carbon with hydrochloric acid removes excesses of non-alloyed metal oxide and leaves on the support the platinum-transition metal alloy. At that time alloy formation, which is still in habit for PAFC electrocatalysts had the main purpose of catalyst stabilisation. It is known today, that on Pt-transition metal alloys also adsorption of oxygen and its catalytic activation is enhanced compared to pure platinum. Therefore the alloy catalyst is not only more stable but also additionally more active because due to alloying the electronic structure of platinum is changed in a way that favours O_2-adsorption on platinum. In the context of reformate and alcohol consuming fuel cells alloy formation and catalyst formulations of binary and ternary composition became indispensable because cocatalysts are needed to oxidize carbon monoxide and other, strongly adsorbed oxidation- and oxidative degradation products of methanol or the higher alcohols together with hydrogen[38,39]. Ralph and Hogart[40], two scientists of Johnson Matthey published the history of particle stabilisation by alloying (for the cathode) and CO–resistance enhancement by alloying (for the anode) till 2001 and Thompson[41] published a respective article in the Handbook of Fuel Cells.

The Bönnemann method[42]

Preparing nanodisperse electrocatalysts which are composed of two, three or even more elements, demands that the preparation method produces not a mixture of crystals of the different elements but a well defined molecular mixture – if possible well defined alloys of the elements in the electrocatalyst particles of nanometer size. By precipitation from aqueous solutions this cannot be attained. Therefore, recently the procedure of Bönnemann became very popular. It is essentially based on reductive precipitation of metals from their salt solutions in aprotic media by a borohydride, a very strong reductant. The intention is the forced codeposition of metals irrespective of their redox potential or different nobleness respectively. The tetrabutyl ammonium cation is a strong surfactant that adsorbs on the precipitated crystallites and prevents their growing beyond a size of between 2 and 3 nm. The result is a nanodisperse material in the form of a sol, which then is anchored by adsorption on active carbon as the usual support. Effectively the reductant is tetrabutyl-tridodecyl-borohydride $N(but)_4\ HB(C_{12}H_{25})_3$. Precipitation for instance of a 1:1:1 mixture of Pt, Ru and W is performed in tetrahydrofuran solution containing dissolved H_2PtCl_6, $RuCl_3$ and WCl_3 in equimolar amounts[43]. By this method almost any desired mixture of elements in any desired molecular ratios can be produced. However, recent investigations show, that not always the desired mixture on molecular level can be obtained as the different reducibility of compounds of different elements occurs sometimes with different rate, so that in the precipitate a certain segregation of the elements is non-voluntarily obtained. Therefore it is clear, that mixed electrocatalysts produced by the Bönnemann method must always be investigated, whether alloys or segregated nanoparticles of variable compositions have been obtained and what is their microstructure and elemental composition.

In Brazil, the electrocatalysts produced by the Bönnemann method with binary, ternary and quaternary compositions have been studied at IPEN/CNEN-SP[44-50](Instituto de Pesquisas Energéticas e Nucleares). Other methodologies of electrocatalysts preparation have also been studied and developed at IPEN/CNEN-SP[51-55] and IQSC/USP[56-61] (Instituto de Química de São Carlos, Universidade de São Paulo).

Means and methods characterizing dispersed platinum and platinum alloy catalysts

Cyclovoltammetry as a method to characterize the electrochemical properties and electrocatalytic potential of active carbon supported nanodisperse electrocatalyst can be applied in a similar manner as is usual for solid electrodes. It is possible to fix the catalyst on glassy carbon by a submicrometer layer of Nafion[62]. This, however, allows only a measurement on short term for screening the most potent formulations among a preselection of a number of different but similar catalyst formulations. The ultimate electrochemical characterization is the long-term performance test in real fuel cells under typical operation conditions. Here long-term means at least several hundred hours, if not more than 1000 h. For research and development, however, many questions concerning the nanostructure of the electrocatalyst must be asked and answered as:

i) Size and size distribution of the catalysts.

ii) Are the components in binary and ternary catalyst formulations attributed to Pt in a form of alloy?

iii) Are the additives evenly distributed on the support and in what chemical form and environment and what is their valency?

iv) If not alloyed, are the additives present in well-defined crystalline phases or are they X-ray amorphous? And how are they spatially distributes.

The most important method to answer these questions is by Transmission Electron Microscopy (TEM). This method fails with X-ray amorphous material but with well-crystallized catalysts it allows for size and size distribution and even determination of lattice parameters. X-ray diffraction according to Debye-Scherrer answers almost the same questions as widening of the refraction signals gives information about the size of the refracting particles. Another method allowing gross analytic identification of the elements and their relative amounts in the catalyst is XPS (X-ray Photoelectron Spectroscopy) and EDX (Energy Dispersive X-ray Spectroscopy). These methods are usually integrated in scanning electron microscopic equipment[63]. All these methods are typical ex-situ methods as they are performed in separate vacuum-apparatus. In-situ characterisation of the solid state properties of the electrocatalyst is only possible by X-ray absorption of "white" X-ray light which is only available in the form of synchrotron-radiation[64]. Although theory and practice of X-ray Absorption Spectroscopy (XAS) are complex and too much specialised to be treated in the context of this article it should be stressed that a great many questions in particular questions ii), iii) and iv) can be answered by the different forms of XAS. The second in-situ method is IR-Absorption Spectroscopy, which tells many things about specifically adsorbed species but almost nothing about the chemistry and physics of the adsorbent, the catalyst or parts of it.

FINAL CONSIDERATIONS

What will be the technological future of low temperature fuel cells and the respective Research and Development into electrocatalysts and electrocatalysis? For the time being, a certain deceleration of research and development is observed because the hopes for a fast evolving fuel cell automobile market could not be fulfilled. But the task of catalyst research, development and fabrication for low temperature fuel cells is far from being finished. The salient point with fuel cell cars was not technical feasibility but costs – which postponed fuel cell development for cars to the late twenties – and then it will be hydrogen/air not methanol reformate/air cells. Nevertheless with so-called portables running on direct methanol cells, APUs (auxiliary power sources for heavy duty vehicles, ships and planes) running on reformate from gasoline and domestic electricity and heat cogeneration based on natural gas there is ample demand for better and more stable anodic and cathodic electrocatalysts. Small portable fuel cells are operated on liquid methanol (more exactly approx. 1 mol L^{-1} aqueous solutions of methanol). Portables are small cells with electric power of 10 to 100 W, which supply camcorders, PCs and other electronic devices. Portables are in this specialised field with costs of from 15,000 to 18,000 USD/kW cost-effective enough to compete with high-valued batteries because their capacity is remarkably higher (charge lasts for approx. a day instead of 3 to 4 h). In the Internet there are some addresses as for instance Smart Fuel Cell® or Oksolar®, to name only two, which testify commercial activities and success.

Auxiliary Power Units (APU) are another interesting option for cars, ships and aeroplanes, which are operated on reformed gasoline or Diesel. They are supposed to substitute heavy and expensive lead acid batteries. For them the same or very similar catalyst formulations would be needed as for reformate powered cells. Finally domestic power sources, which provide electricity and heat for household fired with natural gas may become an option in the future.

For all these purposes PEM – cells have been and still are being developed. There are from the technical and fuel point of view two very different lines of development: PEMFCs for portables with aqueous methanol solutions as fuel which work at close to ambient temperature and PEMFCs cells for APUs, domestic and other stationary power and heat generation which work on reformate gas at enhanced (though low) temperature around 80 °C or somewhat higher. The demands with respect to the anodic electrocatalyst are very different for these two different technologies. Using as fuel aqueous methanol solution, the stability with respect to temperature needs not to be very high, but long-term stability together with stability against frequent current interruption, fuel starvation and voltage-cycling is very important. Additionally the cathode poses a particular problem. With liquid methanol at the anode, substantial amounts of methanol are leaking to the cathode whose performance is severely impaired by methanol poisoning. There are today interesting approaches to make the cathode less sensitive towards methanol poisoning by applying Ru and Pt containing Chevrel phases – but still the state of the art is rudimentary in this respect and the same holds with the anode catalyst, where still nothing better than Pt/Ru is being applied.

PEM cells for domestic use or for APUs working on reformate can still be improved by more sophisticated anodic electrocatalysts as discussed in this article. It is therefore expected, that intensive R&D research will continue on the still relatively young field of fuel cell electrocatalysis and that many innovations and advances are still ahead. Also production technologies must be developed for new catalysts.

Very important is it to take into account, what will be the advances in membrane-technology in the near future. Intensive work worldwide aims in finding a substitute for the usual Nafion membrane and to introduce less solvated ionomers into fuel cell technology in order to raise the working temperature of the gas-operated cell substantially above 100 °C (even to 200 °C). Clearly, higher operating temperatures demands new electrocatalysts. We do now know a lot about activity enhancement by alloying and this knowledge can also be accounted for in theoretical chemistry – but this has not yet predictive power, so that still experimentation, flanked by the marvellous extended analytical methods will be the usual tools of research and development.

Last but not least it should be mentioned that ethanol is a special and typical fuel option for Brazil. Be it reformate from ethanol for PEM-cells or direct anodic oxidation of ethanol in PEM-cells, for both purposes highly active and selective electrocatalysts are indispensable[65]. In Brazil, the direct anodic oxidation of ethanol has been studied at IPEN/CNEN-SP[53-55] and IQSC-USP[66,67], using electrocatalysts prepared by different methodologies. Pt/Sn electrocatalyst has been shown a performance superior to that of Pt/Ru electrocatalyst for direct anodic oxidation of ethanol (Figure 8)[68].

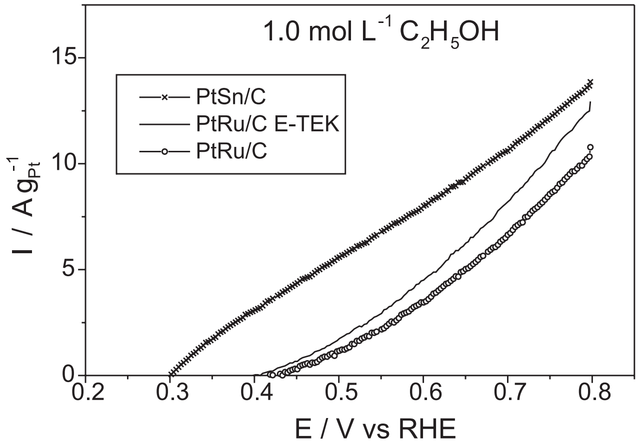


***Figure 8**. Cyclic voltammetry of PtRu/C and PtSn/C electrocatalysts (20wt%, Pt:Me molar ratio 1:1) prepared by alcohol-reduction process and the commercial PtRu/C E-TEK electrocatalyst (20wt%, Pt:Ru molar ratio 1:1) in 0.5 mol L^{-1} H_2SO_4 containing 1.0 mol L^{-1} of ethanol with a sweep rate of 10 mV s^{-1}, considering only the anodic sweep*

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REFERENCES

1. Carrette, L.; Friedrich, K. A.; Stimming, U.; *Fuel Cells* **2001**, *1*, 5.
2. Stull, D. R.; Prophet, H.; *Janaf Thermochemical Tables*, 2nd ed., US National Bureau of Standards: Washington, 1971.
3. Barin, I.; Knacke, O.; *Thermodynamical Properties of Inorganic Substances*, Springer Verlag: Berlin, 1973
4. Kauffmann, G. B.; *Platinum Metals Rev*. **1999**, *43*, 122.
5. Wendt, H.; Rausch, S.; Borucinski, T.; *Adv. Catal*. **1994**, *40*, 87.
6. Wendt, H.; Kreysa, G.; *Electrochemical Engineering, Science and Technology in Chemical and Other Industries,* Springer: Berlin, 1999, ch. 4 and 10.
7. Kemp, F.S.; George, M. A.; *US pat. 3,857,737* **1974**.
8. Petrov, H. G.; Allen, R.J.; *US pat. 3,992,512* **1976**.
9. Kinoshita, K.; Stonehart, P. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M.; Conway, B. E., eds.; Plenum Press: New York, 1977, vol. 12.
10. Stonehart, P.; *Ber. Bunsen Phys. Chem*. **1990**, *94*, 913.
11. Kinoshita, K.; *Carbon – Electrochemical and Physical Properties*, Wiley and Sons: New York, 1987.
12. Bacon, F. T.; *Electrochim. Acta* **1969**, *14***,** 569.
13. Ketelaar, J. A. A. In *Fuel Cell Systems;* Blomen, L. M. M. J.; Mugerwa, M. N., eds.; Plenum Press: New York, 1993.
14. Winsel, A.; Richter, G. J. In *Alkaline Fuel Cells in Electrochemical Hydrogen Technologies*; Wendt, H., ed.; Elsevier: Amsterdam, 1990
15. Watkins, D. S. In ref. 13.
16. Strasser, K.; *J. Electrochem. Soc*. **1980**, *127*, 2172.
17. Steele, B. C. H.; Heinzel, A.; *Nature* **2001**, *414*, 345.
18. Neergat, M.; Friedrich, K. A.; Stimming, U. In *Handbook of Fuel Cells – Fundamentals, Technology, Applications*; Vielstich, W.; Lamm, A.; Gasteiger, H. A., eds.; J. Wiley & Sons: New York, 2003, vol. 4, chap. 63
19. Acres, G. J. K.; Frost, J. C.; Hards, G. A.; Potter, R. J.; Ralph, T. R.; Thompsett, D.; Burstein, G. T.; Hutchings, G. J.; *Catal. Today* **1997**, *38*, 393.
20. Roth, C.; Goetz, M.; Fuess, H.; *J. Appl. Electrochem*. **2001**, *31*, 793.
21. Trasatti, S.; *Electrochim. Acta* **2003**, *48*, 3729.
22. Debe, M. K. In ref. 18, vol. 3, chap. 45.
23. Vielstich, W. In ref. 18, vol. 2, chap. 14.
24. Liu, P.; Norskøv, J. K.; *Fuel Cells* **2001**, *1*, 192.
25. Liu, P.; Logadottir, A.; Norskøv, J. K.; *Electrochim. Acta* **2003**, *48*, 3731.
26. Hamann, C. H.; Hammett, A.; Vielstich, W.; *Electrochemistry*, Wiley-VCH: Weinheim, 1998.
27. Goetz, M.; Wendt, H.; *Electrochim. Acta* **1998**, *43*, 3637.
28. Samjeske, G.; Wang, H.; Loftler, T.; Baltruschat, H.; *Electrochim. Acta* **2002**, *47*, 3681.
29. Binder, H.; Köhling, G.; Sandstede, G.; *From Electrocatalysis to Fuel Cells*, University of Washington Press: Seattle, 1972.
30. Friedrich, K. A.; Geyzers, K-P.; Linke, U.; Stimming, U.; Stumper, J.; *J. Electroanal. Chem*. **1996**, *402*, 123.
31. Watanabe, M. In ref. 18, vol. 2, chap. 28.
32. Gasteiger, H. A.; Marcovic, N. M.; Ross, P. N.; *J. Phys. Chem*. **1995**, *99*, 8945.
33. Trasatti, S.; *Electrochim. Acta* **1984**, *29*, 1503.
34. Tanata, A.; Kanamura, K.; Adzic, R.; Cahan, B.; Yeager, E.; *Proc.-Electrochem. Soc.* **1990**, *90-1*, 969.
35. Spinacé, E. V.; Neto, A. O.; Vasconcellos, T. R. R.; Linardi, M.; *Br. Patent INPI-RJ* PI0304121-2, **2003**.
36. Jalan, V. M.; *US pat. 4,202,934* **1980**.
37. Mukerjee, S.; Srinivasan, S. In ref. 18, vol. 2, chap. 34.
38. Torresi, R. M.; Wasmus, S. In ref. 18, vol. 2, chap. 15.
39. Iwasita, T.; *Electrochim. Acta* **2002**, *47*, 3663.
40. Ralph, T. R.; Hogarth, M. P.; *Platinum Metals Rev*. **2002**, *46*, 117.
41. Thomsett, D. In ref. 18, vol. 3, chap. 37.
42. Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Fretzen, R.; Joussen, T.; Köppler, R.; Korall, B.; Neiterle, P.; Richter, J.; *J. Mol. Catal*. **1994**, *86*, 129.
43. Goetz, M.; Wendt, H.; *J. Appl. Electrochem*. **2001**, *31*, 811.
44. Neto, A. O.; Franco, E. G.; Aricó, E. M.; Linardi, M., Gonzalez, E. R.; *International Workshop on Ceramic & Metal Interfaces*, Oviedo, Spain, 2002.
45. Franco, E. G.; Oliveira Neto, A.; Linardi, M.; Aricó, E.; *J. Braz. Chem. Soc.* **2002**, *13*, 516.
46. Neto, A. O.; Franco, E. G.; Aricó, E. M.; Raimundo, C. P.; Linardi, M.; *XV Congresso da Sociedade Ibero-Americana de Eletroquímica*, Évora, Portugal, 2002.
47. Oliveira Neto, A.; Franco, E. G.; Aricó, E.; Linardi, M.; Gonzalez, E. R.; *J. Eur. Ceram. Soc*. **2003**, *23*, 2987.
48. Neto, A. O.; Franco, E. G.; Aricó, E. M.; Spinacé, E. V.; Linardi, M.; *Fuel Cells Science and Technology,* Amsterdam: Netherlands, 2002.
49. Franco, E. G.; Aricó, E.; Linardi, M.; Roth, C.; Martz, N.; Fuess, H.; *Mater. Sci. Forum* **2003**, *416*, 4.
50. Franco, E. G.; Neto, A. O.; Raimundo, C. P.; Aricó, E. M.; Linardi, M.; *53rd Annual Meeting of the International Society of Electrochemistry*, Dusseldorf, Germany, 2002.
51. Spinacé, E. V.; Oliveira Neto, A.; Franco, E. G.; Linardi, M.; Gonzalez, E. R.; *Quim. Nova* **2004**, *27*, 648.
52. Neto, A. O.; Franco, E. G.; Spinacé, E. V.; Linardi, M.; *54th Annual Meeting of the International Society of Electrochemistry*, São Pedro, Brasil, 2003.
53. Spinacé, E. V.; Neto, A. O.; Linardi, M.; *J. Power Sources* **2003**, *124*, 426.
54. Spinacé, E. V.; Neto, A. O.; Linardi, M.; *J. Power Sources* **2004**, *129*, 121.
55. Spinacé, E. V.; Neto, A. O.; Vasconcelos, T. R. R.; Linardi, M.; *J. Power Sources* **2004**, *137*, 17.
56. Castro Luna, A. M.; Camara, G. A.; Paganin, V. A.; Ticianelli, E. A.; Gonzalez, E. R.; *Electrochem. Commun*. **2000**, *2*, 222.
57. Lizcano-Valbuena, W. H.; Souza, A.; Paganin, V. A.; Leite, C. A. P.; Galembeck, F.; Gonzalez, E. R.; *Fuel Cells* **2002**, *2*, 159.
58. Colmati Jr., F.; Lizcano-Valbuena, W. H.; Camara, G. A.; Ticianelli, E. A.; Gonzalez, E. R.; *J. Braz. Chem. Soc*. **2002**, *13*, 474.
59. Camara, G. A.; Giz, M. J.; Paganin, V. A.; Ticianelli, E. A.; *J. Electroanal. Chem*. **2002**, *537*, 21.
60. Lizcano-Valbuena, W. H.; Paganin, V. A.; Leite, C. A. P.; Galembeck, F.; Gonzalez, E. R.; *Electrochim. Acta* **2003**, *48*, 3869.
61. Lizcano-Valbuena, W. H.; Azevedo, D. C.; Gonzalez, E. R.; *Electrochim. Acta* **2004**, *49*, 1289.
62. Schmidt, T. J. In ref. 18, vol. 2, chap. 22.
63. Hoster, H. E.; Gasteiger, H. A. In ref. 18, vol. 2, chap. 18.
64. Adzic, R. R.; Wang, J. X.; Ocko, B. M.; McBreen, J. In ref. 18, vol. 2, chap. 20.
65. Lamy, C.; Belgsir, E. M.; J-M. Leger, J-M.; *J. Appl. Electrochem*. **2001**, *31*, 799.
66. Oliveira Neto, A.; Giz, M. J.; Perez, J.; Ticianelli, E. A.; Gonzalez, E. R.; *J. Electrochem. Soc*. **2002**, *149*, A272.
67. Souza, J. P. I.; Queiroz, S. L.; Bergamaski, K.; Gonzalez, E. R.; Nart, F. C.; *J. Phys. Chem. B* **2002**, *106*, 9825.
68. Spinacé, E. V.; Oliveira Neto, A.; Vasconcelos, T. R. R.; Linardi, M.; *Abstracts of the VI Encontro Regional de Catálise, Americana*, Brasil, 2004.