Electrocatalysis

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Abstract | Electrocatalysis is a core field of interfacial science because it involves enhancement of reaction rates as in the case of heterogeneous catalysis, with an additional control through the variation of electrode potential. Electrocatalytic rates are influenced by the electrode potential either directly or indirectly. Because of increasing significance of green chemistry and clean energy with an intimate relationship between heterogeneous electrocatalysis and electrochemical energy conversion (batteries and fuel cells), the field of electrocatalysis has grown rapidly. In this article, basic concepts of electrode kinetics to assess electrocatalysis, and catalytic aspects of a few important electrochemical reactions are reviewed.

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Introduction

Electrochemistry is a fascinating field for both fundamental and applied studies. Electronic charge is considered as a versatile reducing or oxidizing agent for a variety of clean and efficient chemical reactions. An electrochemical reaction involves transfer of electronic charge across the interface formed between an electrode and an electrolyte, which leads to an oxidation or a reduction reaction. By proper control of the potential, the electrode can be used as a variable free energy source (or sink) of electrons. Electrons crossing the electrode-solution interface can be determined with high sensitivity by measuring current. Under the present threat of fast depletion of natural resources of fossil fuels and increasing environmental pollution, electrochemistry offers alternate routes of energy conversion comprising uniquely green, efficient and convenient reactions. Some chemicals are manufactured now via electrochemical route and there is even expanding dependence on this subject for several applications. This article provides a brief overview of electrocatalysis of a few selected electrochemical reactions.

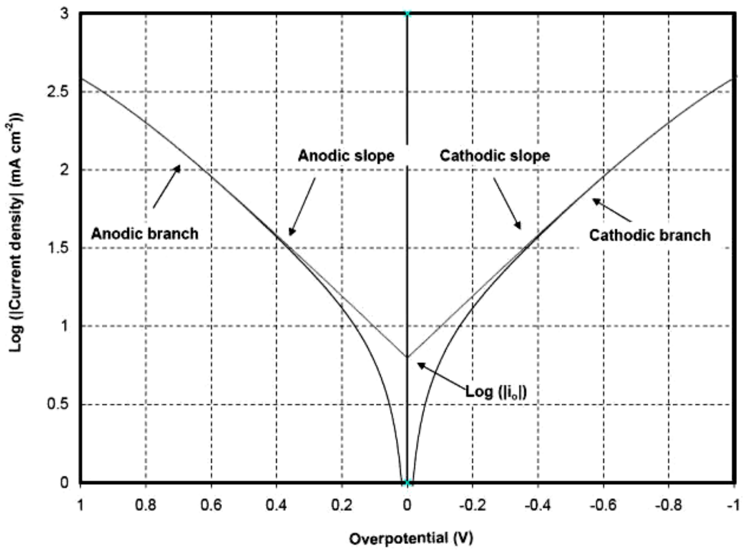
Electrode kinetics and electrocatalysis

Electrochemical reactions which occur at interfaces and involve transfer of electrons can be classified as a branch of heterogeneous reactions [1]. The electrochemical reactions differ from chemical reactions in two ways [2]: (i) Electrochemical reactions do not take place by means of collisions between the reactants unlike in the case of chemical reactions. Thus the entropy of activation, which is associated with the formation of a transitional state between the reactants in chemical reactions, does not have the same significance in electrochemical reactions because it involves entropic considerations of the reactants separately and the electrified surface; and (ii) chemical reactions generally involve heat, but the energy involved in electrochemical reactions is in the form of electrical energy but not heat. As a consequence of this, energy conversion by means of electrochemical devices (batteries and fuel cells) does not involve the Carnot limitation.

Among several properties required to understand electrochemical reactions, potential (E) and current (I) are important [3, 4]. Let us consider the following general reaction:

$$\mathrm{O} + ne^- \rightleftarrows \mathrm{R} \tag{1}$$

Figure 1: Typical Tafel plots and evaluation of kinetic parameters.



where O is the oxidized species, R is the reduced species and n is the number of electrons exchanged between O and R. The Gibbs free energy change (ΔG) of the reaction is related to the electrode potential as in Eq. (2).

$$\Delta G = -nFE \tag{2}$$

where F is the Faraday's constant. The relationship between E and concentrations of species O and R is given by Nernst equation (Eq. 3)

$$E = E^{o} - (RT/nF)\ln([\mathrm{O}]/[\mathrm{R}]) \tag{3}$$

where [O] and [R] are the concentrations of O and R, respectively, E^{o} is the standard electrode potential, R is the gas constant and T is the temperature.

The current is equal to the change in charge with time:

$$I = (\mathrm{d}Q/\mathrm{d}t) \tag{4}$$

where Q is the charge and t is the time. The rate of a reaction is generally expressed as in Eq. (5)

$$\text{rate } = (\mathrm{d}N/\mathrm{d}t) \tag{5}$$

where N is the number of moles. Because the electrochemical reactions are heterogeneous, the rate depends on the area of the electrode (A), and it is given by Eq. (6)

$$rate = I/(nFA) = i/(nF) \tag{6}$$

where i is current density (equal to I/A). The general expression connecting current density and potential is known as Butler–Volmer equation.

$$\begin{aligned} i = i_0[&(C_0/C_0^{*})\exp(-\alpha nF\eta/(RT)) \\ &-(C_\mathrm{R}/C_\mathrm{R}^{*})\exp((1-\alpha)nF\eta/(RT))] \end{aligned} \tag{7}$$

where C_0 and C_0^{*} are the concentrations of O at the electrode surface and bulk of the electrolyte, respectively; $\mathrm{C_R}$ and $\mathrm{C_R^{*}}$ are the concentrations of R at the electrode surface and bulk of the electrolyte, respectively, α is the transfer coefficient, η ($= E - E_{eq}$) is the overpotential, E is the electrode potential when current I flows through the electrode, E_{eq} is the equilibrium potential corresponding to zero current and i_0 is the exchange current density. The exchange current density is related to the standard rate constant (k^0) as,

$$i_0 = nFk^0 C_\mathrm{O}^{*(1-\alpha)} C_\mathrm{R}^{*\alpha}. \tag{8}$$

With efficient mass transfer, the concentrations of the species at the electrode surface and bulk electrolyte are considered equal, and therefore the Butler–Volmer equation reduces to,

$$\begin{aligned} i = i_0[&\exp(-\alpha nF\eta/(RT)) \\ &-\exp((1-\alpha)nF\eta/(RT))]. \end{aligned} \tag{9}$$

This equation describes the current-overpotential characteristics of an electrochemical reaction with electron-transfer step as the rate determining step.

The nature of Butler–Volmer equation (Eq. (9)) is the same as the Tafel equation

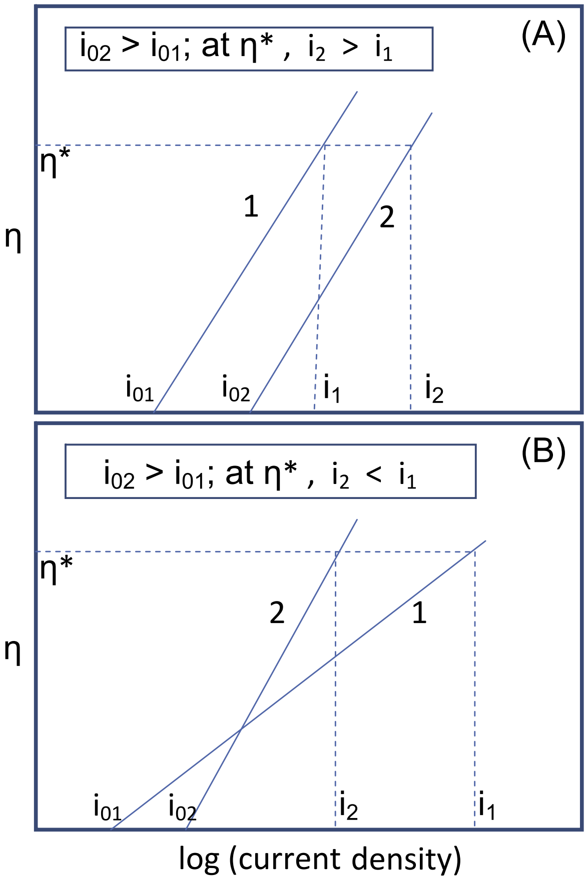
$$\eta = a + b\log i \tag{10}$$

where a and b are constants, which are related to i_0 and α . The parameters i_0 and α are known as the kinetic parameters of electrochemical reactions, which are evaluated from log i versus η graphic representation, generally known as the Tafel plot (Fig. 1).

In case, the electrochemical reaction proceeds with fast electron-transfer usually mass transfer at the electrode/electrolyte interface becomes the rate determining step. Among diffusion, migration and convection, which decide the mass transfer, diffusion can be made as the rate determining step by suitable modification of the experimental conditions. Diffusion related electrochemical reactions are understood on the basis of Fick's laws of diffusion.

Electrocatalysis is a process event or factor by which the rate of electrochemical reaction increases [5–11]. The implications of electrocatalysis are important in industry since it implies production

Figure 2: Typical Tafel plots for comparison of catalytic activities of two electrodes (1 and 2), (A) with similar Tafel slopes and (B) with different Tafel slopes.



increment at lower cost [11]. The generally accepted definition of electrocatalysis is the effect of the electrode material on the reaction rate [8]. This involves the concept of lowering of the activation energy and/or change in reaction mechanism. The effect of electrode material can be real or apparent, depending on the factors influencing. If electronic factors prevail, i.e., if the origin is in the surface structure and chemical composition of the material, this is real electrocatalysis. If the origin of the effect is related to the increase in surface area of the electrode material, this is known as apparent electrocatalysis.

From practical view points, it is obvious that increasing the amount of energy obtained from a fuel cell, for instance, depends on the overpotentials at electrode solution interface. This is also true for any electro synthetic product, because the cost of producing a certain amount of substance is proportional to the total amount of electrical energy needed, which also depends on the overpotentials of the electrochemical reactions. The change in overpotential ($\Delta\eta$) of a reaction at a given current density with two different exchange current densities (i_{02} and i_{01}) can be derived from Eq. 9 as:

$$\Delta\eta = -(RT/nF)ln(i_{02}/i_{01}). \qquad (11)$$

If the electrode process has enhanced exchange current density from i_{01} to i_{02} by changing the electrode of poor electrocatalysis to a better electrocatalyst, the overpotential decreases by $\Delta\eta$. This is based on the assumption that the Tafel plot has the same slope on both the electrode materials as shown schematically in Fig. 2A. However, Eq. (11) is invalid in case there is a change in Tafel slope by changing the electrode material as shown schematically in Fig. 2B. An increase in the exchange current density with increased Tafel slope indicates retardence of the electrochemical reaction at a given current density. While the first procedures of assessing electrocatalysis (Fig. 2A) may be useful for theoretical calculations, the second procedure (Fig. 2B) directly throws light on electrocatalysis in practice.

Electrocatalysis of a few important electrochemical reactions is briefly reviewed below.

Hydrogen evolution and oxidation reactions

The reversible electrochemical reaction

$$H^+ + e^- \rightleftharpoons \frac{1}{2}H_2 \quad E^0 : 0.0V \qquad (12)$$

takes place at an electrode surface. The electrocatalytic activity of the electrode surface, which determines the reaction rate, depends on its chemical composition. This is one of the simplest and widely studied reactions. It is generally accepted that there are three possible reaction steps in the hydrogen evolution reaction (HER) in acidic media (forward process of reaction 12) [12–16]

$$H^+_{aq} + e^- \rightarrow H_{ad} \qquad (13)$$

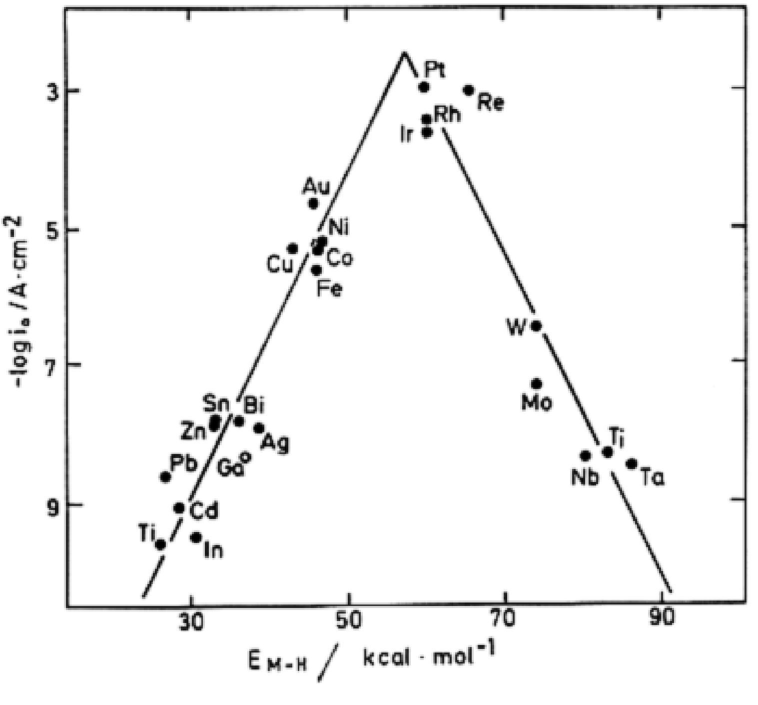
$$2H_{ad} \rightarrow H_2 \qquad (14)$$

$$H_{ad} + H^+_{aq} + e^- \rightarrow H_2. \qquad (15)$$

The first step (reaction 13), known as Volmer reaction involves reduction of H^+_{aq} resulting in the formation of H atom adsorbed on the electrode surface (H_{ad}). Two such H_{ad} atoms can combine together to form a H_2 molecule in Tafel reaction (reaction 14), or else H^+_{aq} ion can get reduced with a simultaneous combination with H_{ad} to produce H_2 in Heyrovsky reaction (reaction 15). The catalytic action of the electrode surface is to adsorb H_{ad} after reaction of protons from solution with electrons from the electrode, and to allow for the formation of molecular hydrogen. The elctrocatalytic activity, which depends on the composition and surface structure of the electrode, is characterized by the exchange current density, i_0 (Eq. 7), which is proportional to the standard rate constant. Usually, i_0 is measured by recording current potential curves under fast mass-transport conditions. Kinetic data for HER are empirically found to correlate with thermodynamic properties. A logarithmic plot of i_0 for various electrodes versus the respective metal–hydrogen bond strength provides a curve known as volcano curve (Fig. 3) [12, 12A]. The two branches of volcano curves are separated at hydrogen chemisorption energy of 0.24 eV [12], which corresponds to the highest exchange current density for HER on Pt. This peak of volcano also corresponds to $\Delta G^0_{\text{ad}} = 0$, where ΔG^o_{ad} is standard free energy change for hydrogen adsorption on Pt surface.

Studies on the effect of single-crystal surfaces on HER catalysis throw light on the kinetics of the reaction and local structural properties. The catalytic activity increases from Au(100), Au(111) to A(110) single-crystal surfaces with respective values of i_0 from 0.05, 0.12 and 0.4 μA/cm^2 [12]. A systematic increase in the defect density leads to larger values of i_0 for Au(110) surface. Pd is an interesting catalyst for HER, although the electrocatalytic activity of Pd is lower than that of Pt, because of absorption of H_2 in bulk metal. Monolayers, sub-monolayers and nanoclusters of Pd avoid absorption effects on kinetics of hydrogen evolution reaction.

Figure 3: Volcano plot of hydrogen evolution reaction (adopted from M.M. Jaksic, J. New Mater. Electrochem. Systems 3 (2000) 167 [12A]).



A catalyst PtPd-WC/C was prepared by microwave heating route and studied for HER in H_2SO_4 electrolytes [13]. The presence of Pd in Pt–WC/C significantly increased catalytic activity on HER, probably due to specific function of Pd for hydrogen storage. Studies on the effect of temperature and concentration of H_2SO_4 suggested that 313 K was the most appropriate temperature for achieving a maximum catalytic activity of the catalyst with increasing concentration of H_2SO.

The coverage and pseudocapacitance behavior of overpotential-deposited (OPD) H species in the cathodic HER at Pt electrode were studied by a potential-decay method, coupled with prior steady-state current measurements in acid and alkaline electrolytes [14]. The OPD hydrogen coverage was larger in acidic than in alkaline solutions. The experimentally derived H coverages were quantitatively related to Tafel slopes for the HER and the electrocatalytic behaviour of the reaction at Pt. The reaction mechanism of HER on Pt was the discharge step followed by the parallel recombination and electrochemical desorption steps. In acid solutions, the discharge step was at quasi-equilibrium and recombination step contributed to the reaction rate at low overpotentials. As overpotential increased, the electrochemical desorption step became more dominant. The mechanisms and electrocatalytic activity of Pt for HER were shown to strongly depend on the activity or the cleanliness of the electrode surface. Impurities were reportedly blocked the active sites for the discharge step. Anodic pulsing was found as an effective and convenient way of reactivating poisoned Pt electrode.

Kinetics of HER on sub-micron size particles of Co, Ni, Pd and Co–Ni alloy were studied by Elumalai et al [16]. Powders of Co, Ni, Pd and Co–Ni alloy were prepared by reduction of the corresponding metal malonates by ethylene glycol and Pd powder by reduction of PdO_x by methanol. DC polarization and AC impedance studies in 6 M KOH electrolyte were carried out using pellet-type electrodes made out of the metal and alloy powders, Steady-state galvanostatic polarization data were linear over three orders of magnitude of current in Tafel plots with a slope close to 120 mV. The values of apparent exchange current density were in the range 1–10 mA/cm^2, which were comparable to the values measured from AC impedance studies. The results suggested that Volmer–Heyrovsky mechanism was valid on these electrodes. Electrodes made from Co–Pd mixtures were found to possess greater catalytic activity for HER than the individual metal powders. A hydrogen storage alloy of the composition $Zr_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2}$ was investigated for corrosion resistance and HER kinetics in KOH electrolytes of varying concentrations by Rodrigues et al [16A]. Activation of the electrode by absorption of H_2 took place after a prolonged cathodic polarization in the potential range of HER. Before the activation, the alloy electrode was found to undergo corrosion with oxygen reduction as the conjugate reaction. The corrosion current density was found to be independent of KOH concentration and had an average value of 30 $\mu A/cm^2$. After activation, the open-circuit potential of the electrode was shifted to a value which was equal to the reversible potential of HER. The exchange current density values measured from Tafel polarization of HER were marginally higher after activation of the electrode.

Studies on HER in neutral and alkaline electrolytes involve non-Pt based electrocatalysts. Prem Kumar and Sathyanarayana evaluated commercial steels in their plain and sulfidized forms in neutral NaCl electrolytes [17]. Thermal sulfidization of steels was found to be a convenient method of modifying the surface of steels to achieve a reduction in hydrogen overpotential in brine solutions. The carbon steels exhibited greater electrocatalytic activity than the silicon steels and stainless steels. A majority of steel electrodes exhibited a reduction in hydrogen overpotential on sulfidization. Similar to the above studies on modified stainless steel electrodes, Angelo studied on Pt electrode, which was surface-modified by S^{2-} chemisorptions [18]. Tafel polarization experiments in NaOH electrolyte suggested an increase in exchange current density from 61.5 $\mu A/cm^2$ to 158 $\mu A/cm^2$, and a decrease in Tafel slope from 0.180 V/dec to 0.170 V/dec on surface modification of Pt electrode by chemisorbed S^{2-}. The reason for enhanced catalytic activity of Pt–S^{2-} electrode was attributed to an increase in adsorption surface sites.

Macroporous Ni electrodeposits were studied for their electrocatalytic activity for HER in an alkaline electrolyte by Marozzi and Chialvo [19]. It was demonstrated that the active electrode area was conditioned by the presence of occluded hydrogen gas inside the pores. It was shown that electrocatalytic activity was the same for electrodeposits of varying roughness factor. The catalytic activity of macroporous Ni deposits was compared with smooth Ni and Raney–Nickel electrodes. Electrocatalysts composed of different hydrogen storage alloys and nickel–molybdenum coatings were studied for HER [20]. These catalysts exhibited low hydrogen overpotential and also excellent time stability under conditions of continuous as well as intermittent electrolysis. Hydrogen storage alloys mainly served the function of hydrogen absorption and release, and consuming the reverse current through electrochemical discharge reactions during intermitten periods. Electrocatalytic activity of nanocomposite $Ni_{81}P_{16}C_3$ electrode for HER in an alkaline electrolyte was studied by impedance spectroscopy [21]. The nanocomposite was prepared by electrochemical deposition route. Quantitative kinetic information obtained by Tafel, impedance and cyclic voltammetry measurements revealed that as deposited $Ni_{81}P_{16}C_3$ was the most active electrode material in comparison with other compositions for HER.

Investigations on oxidation of H_2 (reverse of reaction 12) assume significance because of its importance in polymer electrolyte fuel cells. H_2 is a fuel, which requires a suitable electrocatalyst at the anode for its oxidation. Pt is the most common catalyst at low temperature [22]. For large scale fuel cells, it is desirable to use fuels reformed from methanol or natural gas. However, the catalytic performance of the anode with conventional pure Pt catalysts operating on the reformates is known to be seriously affected by CO poisoning. Several studies were reported on poisoning against electrocatalytic oxidation of H_2 on Pt in the presence of CO [22, 23].

Oxygen evolution and reduction reactions

The oxygen evolution reaction (OER) is another process studied extensively since it is involves in many electrochemical industrial processes, which include cathodic protection, water electrolysis, metal recovery and photoelectrochemical water oxidation [24]

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-. \qquad (16)$$

Because OER is considerably slower than many other cathodic processes, kinetics of OER limits several electrolysis processes. Conway and Liu studied potential-relaxation transients to derive information on the electroactive, kinetically significant adsorbed intermediate states that are involved in OER at Pt electrodes [25]. For oxidized Pt surfaces, information on the behaviour of surface intermediate states of OER was obtained by evaluation of potential-time transients, following interruption of anodic currents for O_2 evolution. The transients were used to evaluate adsorption pseudo-capacitance associated with intermediate states involved at the oxide–solution interface in the mechanism of OER. Both OH and O at the oxide–solution interface and two or more oxidation states of Pt ions at the surface of the oxide film could act as mediator intermediates in the course of oxidation of H_2O to O_2.

Nano-sized ternary ferrites, with molecular formula $CuFe_{2-x}Cr_xO_4$ ($O \leq x \leq 1$) were prepared and studied as electrocatalysts for OER in alkaline solutions [26]. Partial replacement of Fe by Cr in the $CuFe_2O_4$ spinel lattice was found to increase the electrocatalytic activity towards OER greatly. Electrocatalysis of transition metal oxides for OER was reviewed by Matsumoto and Sato [27]. IrO_2 is a good stable electrode in acid, but it is lower in electrocatalytic activity than RuO_2 for OER. A number of thermally decomposed oxides were studied for OER. By comparing the overpotentials at a current density of 100 mA/cm^2, the electrocatalytic sequence in the alkaline solutions was found to follow $RuO_2 > NiO \simeq IrO_2 > PtO_2 > PdO_2$ for OER. Bockris and Otagawa [28] measured OER on eighteen substituted perovskites containing first row transition metal ions. Reaction rates were measured at equilibrium and at an overpotential of 0.30 V. The rate did not depend on semiconductor type properties. However, it increased as the pH of zero charge increased in an alkaline direction, with decrease of magnetic moment, with decrease of stability of the pervoskite lattice, with decrease of enthalpy of formation of the transition metal hydroxides, and with an increase in the number of d-electrons in the transition metal ion. The correlations between the rate and electronic properties were reportedly consistent with rate determining steps which involve desorption of OH radicals. The electrocatalytic activity increased with increased occupancy of the antibonding orbitals of M–OH.

In direct methanol fuel cells, the electrocatalytic reduction of O_2 (reverse of reaction 15) has to compete with the electrocatalytic oxidation of methanol, which diffuses from the anode to the cathode through the polymer electrolyte membrane. Although Pt is one of the best electrocatalysts for oxygen reduction reaction (ORR), its activity is considerably reduced by methanol crossover [29]. Besides this, reduction in the amount of Pt used as the cathode catalyst assumes significance in several studies [29]. Non-noble metal catalysts such as N-containing complexes of Co and Fe were proposed as Pt substitutes, but their chemical instability was a disadvantage. Electrocatalysis of ORR was investigated on glassy carbon electrode in presence of enzyme catalase [29A]. The reaction on noble metal and carbon electrodes was reviewed by Brito and Sequeira [30]. ORR is also an important reaction in metal–air batteries [31].

Oxidation of methanol

Electrooxidations of methanol and other small organic molecules have gained interest in recent years because of potential applications in fuel cells. Extensive investigations have been directed towards development of direct methanol fuel cells (DMFC). Electrooxidation of methanol was reviewed in several publications [32–40]. The thermodynamic potential for methanol oxidation to CO_2 is very close to the equilibrium potential of hydrogen.

$$\begin{aligned} &\mathrm{CH_3OH} + \mathrm{H_2}O \\ &\quad \rightarrow \mathrm{CO_2} + 6\mathrm{H}^+ + 6e^- \quad E^0 0.02V. \end{aligned} \tag{17}$$

As the reaction involves six electrons, the free energy change of the reaction is very high. As a result the energy density of DMFC is high. However, compared with hydrogen oxidation, methanol oxidation is slower by several orders of magnitude. The total oxidation process consists of several intermediate parallel reactions, which can be formulated as follows [33]:

$$\begin{tikzcd} & \mathrm{CO_{ad}} \arrow[r] & \mathrm{CO_2} \qquad (18) \\ \mathrm{CH_3OH} \rightarrow \text{(adsorbed species)} \arrow[r] & {} \arrow[u] \arrow[d] & \\ & \mathrm{HCHO, HCOOH} \arrow[r] & \mathrm{CO_2}. \qquad (19) \end{tikzcd}$$

These pathways require a catalyst, which should be able to dissociate the C–H bond and facilitate the reaction to produce CO_2 as the final product. Pure Pt surface is known to be the best catalyst for breaking C–H bond. Complete oxidation of CH_3OH to CO_2 takes place via two processes occurring in different potential regions : The first process involves adsorption of methanol molecules on the catalyst surface. Since Pt surface is covered with adsorbed H atoms at the potential of CH_3OH oxidation (reaction 17), adsorption of CH_3OH can begin about 0.20 V where sufficient Pt surface sites become available due to desorption of H atom. The second process requires dissociation of water, which is the oxygen donor of the reaction. On pure polycrystalline Pt, a strong interaction of H_2O with the surface can take place at potentials greater than 0.45 V. Thus, CH_3OH oxidation to CO_2 cannot begin on Pt surface at potentials below 0.45 V. In addition to CO_2 which is the major product formed on electrooxidation of CH_3OH, formic acid and formaldehyde are also formed. The yields of these compounds depend on the experimental conditions such as surface roughness, methanol concentration, time of electrolysis, etc. At room temperature, PtRu alloys are found to be the best catalysts for methanol oxidation.

Electrooxidation of CH_3OH in alkaline media on Pt based anodes was reviewed recently by Spendelow and Wieckowski [34]. Alkaline DMFCs were reportedly suffered from problems associated with carbonation of alkaline electrolytes, but several alternatives were suggested including the use of cells designed to operate with carbonate electrolytes, the use of recirculating electrolytes, and the use of anion-exchange membrane electrolytes. In alkaline electrolytes, both carbonate and formate were detected as products of CH_3OH oxidation. At low potentials, methanol oxidation is a slow reaction. Adsorption of CH_3OH and its dehydrogenation proceed at low potentials also, but the reaction is rapidly poisoned by accumulation of adsorbed CO on the electrode, which is not readily oxidized at low potentials. The coverage by CO during or after methanol adsorption and dehydrogenation was measured by voltammetric oxidation of CO in methanol free solutions. CO was also detected using infrared spectroscopy. On several low-index Pt surfaces, CO was found to be present in relatively minor amounts. The CO coverage during CH_3OH oxidation on Pt in alkaline media varied with the surface structure. Since CH_3OH dehydration is slower on Pt(III) than on Pt(110) or Pt(100), Pt(111) exhibited the lowest steady-state CO coverage of the three basal surfaces. The steady-state CO coverage on Pt(111) in methanol containing solutions is determined largely by the defect density, since defects are the active sites for CO oxidation. Addition of kink-type defects to a Pt(111) surface leads to a lower CO coverage, since these sites promote CO oxidation but not methanol dehydrogenation. In contract, adding step-type defects leads to an elevated CO coverage, since these defects promote methanol dehydrogenation more than CO oxidation. Polycrystalline Pt surfaces, which have a high concentration of domain boundaries and other defects, are more active than either Pt(111) or Pt(110) for methanol oxidation in alkaline media.

Progress in design and characterization of Pt–Ru electrocatalysts for DMFC is reviewed recently by Petrii [37]. Pt–Ru system is more complex than single-element catalysts. The high catalytic activity of Pt–Ru is known as bifunctional mechanism. The Ru centers are responsible for generation of active oxygen species. While Pt centers keep the adsorbed CH_3OH species. The spatial separation of the chemisorbed methanol and oxygen results in combination of these species. For confirming the bifunctional mechanism, a good correlation between the number of Pt–Ru pairs and catalytic activity for CO electrooxidation was reported. The highest activity corresponded to the maximum number of Pt–Ru pairs.

The electrooxidation characteristics of CO, CH_3OH, and formic acid on Pt particles of varying size were investigated by Scheijen et al [38]. The particles were prepared by galvanostatic deposition of Pt on polished polycrystalline Au electrodes. Three surfaces with low, medium and high Pt coverages were generated and characterized by voltammetry and atomic force microscopy. The particle size ranged from 10 to 20 nm in diameter for low Pt surface concentrations, 10 to 120 nm for medium concentrations, and full Pt monolayers for high concentrations. The electrooxidation activity of methanol was found to decrease with the particle size, whereas formic acid oxidation rate increased. Nanoparticles of Pt were electrochemically dispersed uniformly on a conducting polymer modified carbon paper electrode and they were shown to possess a high electrocatalytic activity for methanol oxidation [38A].

Electrooxidation of Cl^- ion

The electrooxidation of Cl^- ion is one of the most studied topics in the field of electrocatalysis owing to its impact on electrochemical technology in the production of chlorine gas, chlorates and perchlorates [41–42]. Electrochemical production of chlorine (reaction 20) and alkali in chlor-alkali industry is one of the great successes of electrochemical technology.

$$2Cl^- \rightarrow Cl_2 + 2e^-. \tag{20}$$

The search for new electrode materials faced success when Beer [43] reported promising properties of the oxides of Pt group metals. The introduction of such anodes into the chlor-alkali industry provoked a technological jump. Coatings of RuO_2 on Ti, which are known as dimensionally stable anodes (DSA), became the most desirable electrodes for Cl_2 evolution reaction [44–46]. These electrodes can be prepared by thermal decomposition of $RuCl_3$ solutions sprayed on Ti substrates. The performance of RuO_2/Ti dimensionally stable anodes was so outstanding that all graphite anodes were replaced by these anodes in a few years of their discovery. Although it was established on a thermodynamic basis that chlorine evolution from aqueous solutions would be impossible in aqueous solutions, it could take place over a restricted range of acidic solutions because of higher overpotential for oxygen evolution reaction on RuO_2 electrodes. The $pH \approx 4$ of the electrolyte is critical because chlorine evolution occurs when pH is below 4, and oxygen evolution occurs at higher pH in NaCl aqueous electrolytes. In fact, oxygen evolution gives rise to local acidification of the solution with consequent shift of this reaction to more anodic potential than the potential of chlorine evolution.

Oxide electrodes prepared by thermal decomposition of suitable precursors consist of porous layers of sintered crystallites. Porosity and crystallite size depend on the calcinations temperature. The rate of chlorine evolution does not follow the increase in surface area of RuO_2 electrodes. Porosity effects are responsible for local acidification of the solution during oxygen evolution. In the pores, the pH is usually very low and insensitive to the external acidity of the bulk solution, a feature which is advantageous for chlorine evolution. Further more, the morphology of the active layer changes with the calcinations temperature and loading level of the catalyst.

Because of a high reversibility on most oxide coated electrodes, Cl_2 reaction is studied by various kinetic parameters, which include Tafel slopes, stoichiometric number, true exchange current, transfer coefficient, order of the reaction and reversible potential. The kinetic parameters are greatly influenced by experimental variables such as porosity and morphology of the anode, specific adsorption of anions, dissolution of Cl_2 gas in the electrolyte, formation of bubbles on the electrode, solution pH, and passivation of the electrode. Because the usual support of activated oxide coated anodes is titanium, the growth of an insulating film can distort the Tafel line. Distortion is usually related to the presence of ohmic drop. Insulating films can form during the preparation of the oxide coating on Ti if the calcination temperature is high. Another possibility is that the support becomes passive during the anodic reaction because of oxygen evolution inside the pores whose depth can reach the underlaying interface.

The mechanism of Cl_2 evolution on oxide electrodes is complicated by specific features of these materials. On all investigated oxides, the reaction order with respect to Cl^- is found to be unity [46]. Typical performance of $RuO_2 + TiO_2$ coated titanium dimensionally stable anode is a current density up to 1.5 A cm^{-2} at an overpotential of 10–40 mV and a coating life-time of several years. These features are of extreme industrial importance when compared with 500 mV of overpotential at a lower current density and a continuous wear rate of 5 g of carbon per ton of chlorine for graphite anodes.

Mozota et al. [47] studied the effect of the nature of oxide films Ir and Ru on the kinetics of Cl_2 evolution. The variations in cyclic programmes of potential changes of Ir and Ru were found to modify the states of oxide films, on these metal anodes, which in turn influence the rates of Cl_2 evolution. Oxide films of controlled thickness were formed on these metals depending on the period of cycling and potential ranges in 0.5 M H_2SO_4 solution. Kinetics of Cl_2 evolution were studied on these oxide films by recording Tafel polarization data in a mixed electrolyte of 1 M KCl and 0.01 M HCl. Chlorine evolution rates were found to increase with increase in thickness of oxide films on Ir and Ru. Evaluation of double-layer capacitance of Ir electrodes grown with different thickness values of oxides indicated that the real areas of the cycled electrodes did not increase with oxide thickness. The increased rates of Cl_2 evolution on modified Ir oxide surfaces were attributed to a real enhancement of the intrinsic electrocatalytic properties of the surfaces for Cl_2 evolution reaction. In the case of Ru metal, kinetic studies for Cl_2 evolution on a monolayer covered metal and multilayer formed after 20 cycles on the metal suggested that the rate of the reaction increased by about 30 times on thicker oxide coated Ru. Electrocatalysis and chlorine evolution reaction of RuO_2 deposited on conductive boron doped diamond electrodes were studied by Ferro and Battisti [48]. Chlorine evolution reaction at the electrode with the lower oxide loading occurred through a spill over mechanism involving RuO_2 particles at which Cl^- ions were discharged. After this step, the adsorbed radical spilled over to the diamond surface as a result of thermal agitation and chlorine molecules were formed. Properties of the oxide electrode materials suitable for chlorine evolution and oxygen evolution reactions were discussed by Trasatti [49]. It was shown that the temperature of preparation of RuO_2, IrO_2, Co_3O_4 and $IrO_2 + RuO_2$ electrodes affected the catalytic activity through the chemical composition and surface area. Under suitable experimental conditions, electrooxidation of Cl^- can also proceed to produce chlorite, hypochlorate, chlorate and perchlorate. PbO_2 is the best known catalyst for elecrooxidation of chlorate to perchlorate [50–53].

Chemically modified electrodes

Until the mid-1970s, the electrodes used for electroanalysis were continued to materials such as carbon, gold, platinum and mercury. Often most of these electrode surfaces encounter specific phenomena, which reduce the applicability of these electrodes for electroanalysis as well as for electrosynthesis [54]. Fouling of the electrode by unwanted precipitation or adsorption processes are known to cause deterioration of the electrode activity. This problem can be controlled by manipulating the chemical nature of the electrode surface. The concept of chemically modified electrodes (CMEs) was first introduced by Murray's group to seize direct control of the chemical nature of the electrode surface [54–57]. By attaching a chemical reagent to the electrode surface, the electrode attains the properties of the attached reagents. If appropriate reagents are chosen, desirable properties such as reagent-based control of the rates and selectivity of electrochemical reactions (i.e., electrocatalysis), freedom from adsorptive and coating effects can be achieved. Chemically modified electrodes are investigated in varied directions, which include synthetic design of electrochemically modified polymers, basic studies of electrocatalysis, electron-transfer kinetics, electrochromics, electroanalysis, photoelectromistry, etc. An important motivation for surface modification is electrocatalysis of a desired reaction in electroanalysis. It is observed that the electrode kinetics of an analyte at a naked electrode surface are slow, so that oxidation or reduction occurs at a potential that is more positive or negative, respectively, than the thermodynamic potential. The large overpotential can be decreased by accelerating the desired reaction with an immobilized mediator as a catalyst. The action of the mediator could be, for instance, the oxidized form of it can be rapidly reduced by the electrode and then its reduced form reacts with the analyte species in solution. Interesting examples of using electrocatalysis for analytical applications include reactions of electrooxidizable analytes dopamine, ascorbic acid and NADH at carbon electrodes. NADH is slowly oxidized at carbon electrodes, and chemically modified carbon electrode catalyzes its oxidation via immobilized mediators [58]. Another problem with NADH is that its oxidation products tend to foul the naked electrode surface.

Conductive polymer modified electrodes are studied for electrocatalysis of redox reactions. Some of these studies include electrodeposition of conductive polymers such as polyaniline or polypyrrole on Pt electrode and study the electrocatalytic effect of the polymer on redox reactions [59–62]. In such studies, the substrate electrode Pt itself is a good catalyst for these reactions and only a marginal electrocatalysis is observed due to the presence of surface modified electroactive polymer. It is more interesting to study the effect of conductive polymer on a non-Pt metal surface, which cannot allow a redox reaction to take place on its naked surface. Common non-Pt metals such as nickel, stainless steel were used as the substrates, and conductive polymers such as polyaniline polypyrrole, etc., were electrochemically deposited. The conductive polymer coated non-Pt metal electrodes were found to catalyze redox reactions, Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ and I^-/I_3^- [59–60]. Electrocatalysis of ascorbic acid was also studied [61].

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