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Review

Electrocatalytic oxidation of small organic molecules in acid medium: Enhancement of activity of noble metal nanoparticles and their alloys by supporting or modifying them with metal oxides

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ABSTRACT

Different approaches to enhancement of electrocatalytic activity of noble metal nanoparticles during oxidation of small organic molecules (namely potential fuels for low-temperature fuel cells such as methanol, ethanol and formic acid) are described. A physical approach to the increase of activity of catalytic nanoparticles (e.g. platinum or palladium) involves nanostructuring to obtain highly dispersed systems of high surface area. Recently, the feasibility of enhancing activity of noble metal systems through the formation of bimetallic (e.g. PtRu, PtSn, and PdAu) or even more complex (e.g. PtRuW, PtRuSn) alloys has been demonstrated. In addition to possible changes in the electronic properties of alloys, specific interactions between metals as well as chemical reactivity of the added components have been postulated. We address and emphasize here the possibility of utilization of noble metal and alloyed nanoparticles supported on robust but reactive high surface area metal oxides (e.g. WO_3, MoO_3, TiO_2, ZrO_2, V_2O_5, and CeO_2) in oxidative electrocatalysis. This paper concerns the way in which certain inorganic oxides and oxo species can act effectively as supports for noble metal nanoparticles or their alloys during electrocatalytic oxidation of hydrogen and representative organic fuels. Among important issues are possible changes in the morphology and dispersion, as well as specific interactions leading to the improved chemisorptive and catalytic properties in addition to the feasibility of long time operation of the discussed systems.

1. Introduction

Development of the science and technology of low-temperature fuel cells (FCs) is a multidisciplinary challenge. Significant progress has been made in this area, but there are still a number of fundamental problems to be resolved not only in fuel cell design but also in the choice of electrode materials and their utilization [1–7]. In particular, FC limitations are connected to (i) the poor activity/stability of conventional electrocatalysts, (ii) the poisoning of electrocatalytically active species by strong adsorption of intermediate products during reaction (i.e. CO during oxidation of alcohols); (iii) slow kinetics of electrode reactions including that of oxygen reduction at the cathode, and complexity and thus low efficiency of the oxidation processes that may be considered at the anode; and (iv) fuel cross-over through the membrane, which depolarizes the cathode and decreases its activity [1–3,8–12]. Moreover, the necessity of cost reduction and improvement of the performance of conventional Pt-based catalysts requires development of multicomponent systems capable of operating at low temperatures, certainly below 150 °C [13] but practically much lower than 100 °C. Therefore, having in mind the overall efficiencies of electrode processes, reaction rates need to be enhanced (i.e. the overvoltages need to be decreased) either by increasing the reaction temperature or by modifying the catalyst composition or structure thus producing a more active electrocatalytic material. By increasing reaction temperature, the poisoning effect of the otherwise strongly bonded CO intermediate diminishes with respect to activity of noble metal catalytic surfaces. On the other hand, performance of the proton-exchange polymer membranes lowers due the reduced ionic conductivities caused by the membrane dehydration at higher temperatures [14].

A common approach to enhancing the reactivity of platinum involves its nanostructuring to produce electrocatalysts of high surface area and dispersion [1–4]. Further optimization of Pt-based electrocatalysts has been achieved through the formation of bi- and tri-metallic alloys such as PtCr and PtCo (oxygen reduction), PtRu (oxidation of methanol), PtPd (oxidation of formic acid), and PtSn

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(oxidation of ethanol). With such systems, that have been recently discussed and reviewed [4–7], enhancement of the Pt catalytic activity has been understood in terms of changes in the electronic nature and morphology of the Pt surface and mutual interactions between alloy-forming metals. In the present review, we concentrate mostly on efficient electrocatalytic systems that poisoning of the Pt catalyst can be diminished by increasing the FC operating temperature and the roughness factor or dispersion of the Pt [1–3]. It has also been demonstrated that efficiency can be further improved by deliberate modification of the electrocatalytic interface or by promotion that utilize robust large-surface-area metal oxides (e.g. WO_3, TiO_2 or ZrO_2) as supports or matrices capable of physically separating metal particles (to diminish their tendency to undergo degradation by agglomeration) in addition to interacting mutually with them, thus affecting their chemisorptive and catalytic properties. Oxides are often thought as insulating or semiconducting materials but certain nonstoichiometric oxides existing in various valance states exhibit conductivity not much lower than that of metals and possess appreciable catalytic activity [15–17]. Among other important issues is the presence of bulk and surface states that affect reactivity of oxide films [18]. It is reasonable to expect that the ideal matrix for dispersed catalytic centers would be reactive toward the fuel studied or its reaction intermediates. Finally, an overall physicochemical stability is an issue as well.

2. Platinum as model catalytic metal

Because of its stability and activity in contact with acid electrolyte, platinum is one of the most used electrocatalysts for oxidation of organic molecules, including electrooxidation of alcohols [11,13,19]. Pt is very active toward C—H bond breaking and dissociative adsorption of alcohol; however, with respect to C—C bond breaking (e.g. in ethanol and longer chain alcohols) some difficulties are observed. During the oxidation of small organic molecules, usually CO or CO-type (CHO) intermediates are formed; they are strongly adsorbed on the Pt catalyst surface thus blocking active sites and poisoning the catalytic material. Therefore, for longer chain alcohols (including ethanol), the complete oxidation to CO_2 is much more difficult than for methanol. Further, the reactions proceed at potentials where CO or other by-products are either chemisorbed or ineffectively oxidized, which results in the development of increased overpotentials and loss of efficiency [11,13,19]. Many fundamental studies have shown that poisoning of the Pt catalyst can be diminished by increasing the FC operating temperature and the roughness factor or dispersion of the Pt [1–3]. It has been demonstrated that efficiency can be further improved by deliberate modification of the electrocatalytic interface or by promotion through introduction of other components [14,20–23]. Clearly, the development of highly active electrocatalysts is of primary importance to further improvement of the FC performance. In this regard, matrices that are characterized by good stabilities, large surface areas, and high proton and electron conductivities [6,7,24,25] are often needed.

3. Pt based alloys and intermetallic compounds in electrocatalysis

Until now, various electrocatalysts including binary and ternary alloys or intermetallic compounds have been investigated to promote electrooxidation reactions [26–30]. Because ruthenium can promote catalyst (Pt) reactivity by water activation and can provide preferential sites for OH-adsorption at low potentials, Ru is one of the most popular components used as a second metal of Pt-based binary electrocatalysts [8,13,19]. It can mitigate CO or CO-type intermediate accumulation on the catalyst surface and lower the potential of oxidation to CO_2. The ratio of Pt to Ru also plays an important role. Although the best results for the oxidation of CO adsorbates at bimetallic Pt–Ru electrocatalysts typically have been obtained where the ratio of Pt to Ru is 1:1, the optimum content of Ru vs. Pt as well as the optimum morphology of the system is still under debate [8,19]. For example, the preferred relative content of Ru (to Pt) was postulated for methanol oxidation to be at the 20% (at.) level [9]. The actual value for the optimum ratio of Ru to Pt is a subject of dispute, but it should be remembered that a mixed bulk face-centered cubic (fcc) PtRu phase (with a statistical distribution of Pt and Ru on the surface and related high bifunctional activity) forms when the relative atomic content of Pt to Ru exceeds 40% [31]. Due to lower stability of Ru component, a proper determination of the surface concentrations of the alloy constituents is very important.

It was also demonstrated that a highly dispersed PtSn catalyst can be as active as PtRu for methanol oxidation [12]. Unlike ruthenium in PtRu, which is largely metallic, tin is unlikely to maintain its metallic state under operating conditions, Sn can be converted to oxygenated species such Sn oxides or hydroxides [21,32]. Recent investigations, however, have revealed that complete ethanol oxidation can be performed effectively on Pt admixed with SnO_x, which suggests that formation of an intermetallic platinum-tin phase is not required in the case of this reaction. It was found that the mechanism and the product distribution during electrooxidation of ethanol were dependent on the tin content, but little as 5% tin was sufficient to enhance this electrocatalytic process [21]. The presence of Sn or SnO_x in the vicinity of Pt seemed to mitigate the otherwise-strong ligand effect, thus weakening the Pt–C interactions responsible for C—C bond splitting in ethanol; under such conditions, acetaldehyde rather than CO_2 will be produced predominantly [19]. Overall, the results concerning PtRu and PtSn electrocatalysts are often contradictory or, at least, open to further discussion. Apparently, the final activity of these systems during the electrooxidation of ethanol is a function of the active-phase dispersion, composition (i.e. the Pt:Me ratio, where Me is Sn, Ru or Sn + Ru), and preparation method [19,30,33].

Utilization of the above-mentioned bimetallic catalytic nanoparticles is often facilitated by the choice of matrix, deposition environment and fabrication procedure. It was shown that out of two systems, PtSn and PtRu, electrodeposited within polyaniline, the latter exhibited higher activity for methanol oxidation [34,35]. Enhancement of methanol oxidation also was observed at a sputtered Pt_3Sn surface, but the magnitude of the effect was lower relative to that observed on PtRu alloys [36]. But under some conditions, carefully and precisely dispersed Sn-containing systems can exhibit higher electrocatalytic activities than PtRu toward methanol electrooxidation [19,37,38]. In these studies, smooth platinum, platinized platinum and PbPt electrodes modified by poly(o-phenylenediamine) were used, and Pt, PtRu and PtSn particles were electrochemically deposited. Although PtRu and PtSn systems are recognized as active and promising for the alcohol FC research (e.g. oxidation of ethanol or ethylene glycol), in practice, reaction products with C—C bonds still appear in sizeable amounts. In other words, dehydrogenation of alcohols and dissociation of C—C and C—O bonds existing in ethanol and higher alcohols still remain as key issues [39].

4. Electrocatalytic systems of trimetallic and more complex alloys

With the goal of producing more functionalized electrocatalytic systems, recent literature reports on alternative Pt alloys including binary systems (e.g. PtPd, PtAu, PtRe, PtW and PtMo) and more complex PtRu- and PtSn-based alloys such as PtRuOs, PtRuSn,

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