

The methanol oxidation reaction on platinum alloys with the first row transition metals The case of Pt–Co and –Ni alloy electrocatalysts for DMFCs: A short review

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Received 13 July 2005; received in revised form 15 September 2005; accepted 22 September 2005

Available online 8 November 2005

Abstract

In recent years there has been much activity in examining Pt alloys with first row transition metals as catalysts materials for DMFCs. In this work, the electrochemical oxidation of methanol on Pt–Co and –Ni alloy electrocatalysts is reviewed. The effect of the transition metal on the electrocatalytic activity of Pt–Co and –Ni for the methanol oxidation reaction (MOR) has been investigated both in half-cell and in direct methanol fuel cells. Conflicting results regarding the effect of the presence of Co(Ni) on the MOR are examined and the primary importance of the amount of non-precious metal in the catalyst is remarked. For low base metal contents, an enhancement of the onset potential for the MOR with increasing Co(Ni) amount in the catalyst is observed, whereas for high contents of the base metal, a drop of the MOR onset potential with increasing Co(Ni) is found. As well as the base metal content, an important role on the MOR activity of these catalysts has to be ascribed to the degree of alloying. © 2005 Elsevier B.V. All rights reserved.

Keywords: Methanol oxidation; Platinum alloy catalysts; Nickel; Cobalt; Direct methanol fuel cell

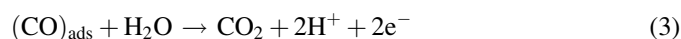
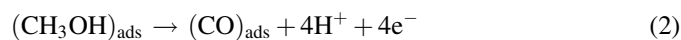
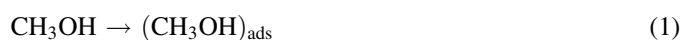
1. Introduction

The use of methanol as energy carrier and its direct electrochemical oxidation in direct methanol fuel cells (DMFCs) represents an important challenge for the polymer electrolyte fuel cell technology, since the complete system would be simpler without a reformer and reactant treatment steps. The use of methanol as fuel has several advantages in comparison to hydrogen: it is a cheap liquid fuel, easily handled, transported, and stored, and with a high theoretical energy density [1–3].

Although a lot of progress has been made in the development of DMFC, its performance is still limited by the poor kinetics of the anode reaction [3–5] and the crossover of methanol from the anode to the cathode side through the proton exchange membrane [6–8].

Methanol oxidation is a slow reaction that requires active multiple sites for the adsorption of methanol and the sites that

can donate OH species for desorption of the adsorbed methanol residues [9]. Methanol oxidation has been extensively investigated since the early 1970's with two main topics: identification of the reaction intermediates, poisoning species and products, and modification of Pt surface in order to achieve higher activity at lower potentials and better resistance to poisoning. The results have been reviewed by several authors [10–12]. The main reaction product is CO₂ [13], although significant amounts of formaldehyde [14,15], formic acid [13] and methyl formate [15,16] were also detected. Most studies conclude that the reaction can proceed according to multiple mechanisms. However, it is widely accepted that the most significant reactions are the adsorption of methanol and the oxidation of CO, according to this simplified reaction mechanism:



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Platinum is the most active metal for dissociative adsorption of methanol, but, as it is well-known, at room or moderate temperatures it is readily poisoned by carbon monoxide, a by product of methanol oxidation. To date, the remedy has been to use binary or ternary electrocatalysts based on platinum, all containing ruthenium as the activity promoting component [17–22]. According to the bifunctional mechanism [23,24], the CO-poisoned platinum is regenerated via a surface reaction between CO- and O-type species associated with ruthenium to yield CO₂. According to the ligand model [12,23,25], instead, the change in Pt electronic properties induced by the presence of Ru renders Pt atoms more susceptible for OH adsorption [23] or even for dissociative adsorption of methanol [12]. But also when Pt–Ru is used as anode electrocatalyst the power density of a DMFC is about a factor of 10 lower than that of a proton exchange membrane fuel cell operated on hydrogen if the same Pt loading is used. Therefore, a number of Ru-alternative elements, showing a co-catalytic activity for the anodic oxidation of methanol, if used either as platinum alloys or as adsorbate layers on platinum, have been investigated [26–33].

The problem of methanol crossover in DMFCs has been extensively studied [6–8,34,35]: methanol adsorbs on Pt sites in the cathode for the direct reaction between methanol and oxygen. The mixed potential, which results from the oxygen reduction reaction and the methanol oxidation occurring simultaneously, reduces the cell voltage, generates additional water and increases the required oxygen stoichiometric ratio. This problem could be solved either by using electrolytes with lower methanol permeability or by developing new cathode electrocatalysts with both higher methanol-tolerance and higher activity for the oxygen reduction reaction (ORR) than Pt. Higher methanol-tolerance is reported in the literature for non-noble metal electrocatalysts based on chalcogenides [35–38] and macrocycles of transition metals [39,40]. These electrocatalysts have shown nearly the same activity for the ORR in the absence as well as in the presence of methanol. However in methanol-free electrolytes, these materials did not reach the catalytic activity of dispersed platinum. Developing a sufficiently selective and active electrocatalyst for the DMFC cathode remains one of the key tasks for further progress of this technology. The current direction is to test the activity for the oxygen reduction reaction in the presence of methanol of some Pt alloys with the first row transition metals which present a higher activity for the ORR than platinum in low temperature fuel cells operated on hydrogen, and use them as DMFC cathode electrocatalysts [41–45]. The improvement in the ORR electrocatalysis has been ascribed to different factors such as changes in the Pt–Pt interatomic distance [46] and the surface area [47]. But the behaviour of binary alloys with respect to electrocatalysis can be better understood in terms of the electronic “ligand effect” and/or the geometric “ensemble effect”. To rationalise these effects it is necessary to know precisely the local concentration and arrangement of both components at the very surface (in contact with the reactants), and also in the sublayers which influence electronically the outer atoms [48]. The electronic effect of elements present in the sublayers is illustrated on PtNi (1 1 1) and Pt₃Fe (1 1 1), which present a quasi-complete Pt surface layer (with more or less Ni or

Fe in the sublayers) and strong modifications of their chemisorptive properties and electrocatalytic performances [48]. This behaviour was attributed to the electronic effect of intermetallic bonding of the alloying component-rich second layer with the top-most Pt atoms. The electrocatalytic behaviour of Pt alloys with increasing contents of the second element can be explained by the model of Toda et al. [49], based on an increase of d-electron vacancies of the thin Pt surface layer caused by the underlying alloy.

The ensemble effects where the dilution of the active component with the catalytically inert metal changes the distribution of active sites, open different reaction pathways [50]. The dissociative chemisorption of methanol requires the existence of several adjacent Pt ensembles [51,52] and the presence of atoms of the second metal around Pt active sites could block methanol adsorption on Pt sites due to the dilution effect. Consequently, methanol oxidation on the binary-component electrocatalyst is suppressed. On the other hand, oxygen adsorption, which usually can be regarded as dissociative chemisorption, requires only two adjacent sites and is not affected by the presence of the second metal.

Pt–Ni and –Co alloy catalysts have been proposed both as methanol-tolerant cathode material and anode material with improved MOR for DMFCs. The choice of Co and Ni to modify Pt electrocatalyst to improve the MOR is due to the lowering of the electronic binding energy in Pt by alloying with these metals, promoting the C–H cleavage reaction at low potential. Moreover, the presence of cobalt or nickel oxides provides an oxygen source for CO oxidation at lower potentials. On the other hand, a higher methanol-tolerance is expected on Pt–Co and –Ni alloy catalysts than on Pt, ascribed to the dilution effect of Pt, hindering the methanol adsorption. Furthermore, these alloys present an improved activity for the oxygen reduction than Pt alone. On the basis of this discrepancy, we will attempt to outline the electrochemical activity for the MOR of Pt–Ni and –Co alloy catalysts.

2. Structural characterization of Pt–Co and –Ni alloys

In the composition range from 0 to 50 at.% Co(Ni), Pt and Co(Ni) form a substitutional continuous solid solution and two ordered phases [53–56]. The dependence of the lattice parameter of the Pt–Co and –Ni bulk alloys on the alloy composition is reported in Fig. 1. In the region of 75 at.% Pt there are face-centered cubic (fcc) superlattices Pt₃Co and Pt₃Ni of the Cu₃Au (L1₂) type. Regular termination of the bulk L1₂ structure normal to the three major zone axes produces a variety of surface compositions, from the pure Pt ((2 0 0) and (2 2 0) planes), 25 at.% Co(Ni) ((1 1 1) plane) to 50 at.% Co(Ni) ((1 0 0) and (1 1 0) planes) [57].

To better understand the relationship between the surface composition and the catalytic activity, it is very important to determine if surface segregation, i.e. enrichment of one element at the surface relative to the bulk, takes place during the preparation of these alloy catalysts. The details of segregation are still not completely understood, especially in the case of segregation in nanoparticles in which the characteristics may differ from those of the bulk. This is not surprising, considering

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