

Review

Theoretical means for searching bimetallic alloys as anode electrocatalysts for direct liquid-feed fuel cells

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Abstract

The present paper reviews the best anode electrocatalysts, mainly the alloys, which have been tested in direct liquid-feed fuel cells fed with methanol, ethanol or formic acid. It attempts to interpret the alloys catalytic behaviours by using the Nørskov and co-workers' theoretical work [A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver, J.K. Nørskov, *J. Mol. Catal. A* 115 (1997) 421; B. Hammer, J.K. Nørskov, *Adv. Catal.* 45 (2000) 71; J. Greeley, J.K. Nørskov, M. Maurikakis, *Annu. Rev. Phys. Chem.* 53 (2002) 319], who proposed surface theories and databases about the metals d-band centre shift and the segregation. It also attempts to suggest new alloys combinations. For example, for the methanol oxidation, the best catalyst is Pt-Ru and the following features make this catalyst stand out: the d-band centre of Pt shifts down what supposes weaker molecules adsorption and Pt strongly segregates. From this analysis, it is suggested that the Pd-Ni alloy may be a potentially good catalyst. Similar interpretations are given for the three fuel cell systems regarded in the present paper.

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Keywords: Direct liquid-feed fuel cell; Electrocatalyst; Alloys; Metal d-band centre; Segregation

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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) shows excellent performance when fed with hydrogen and it would be the best fuel cell if the use of hydrogen were not a key limitation [1]. Hence investigations about the use of methanol, ethanol or formic acid as liquid fuels for PEMFCs have been started on. Compared to hydrogen, methanol is cheaper and, easily handled,

transported and stored. However, it is toxic, inflammable, not a primary fuel and not renewable [2]. Ethanol is attractive, lowly toxic, renewable and easily produced [3]. The main advantage of formic acid is the high electromotive force (1.45 V) of the corresponding fuel cell [4].

The success of the PEMFCs largely depends on two key materials: the membrane and the electrocatalysts [2]. Regarding the anode electrocatalyst, the search for new catalysts is necessary in order to improve the catalytic performances and the resistance towards poisoning. A strategy focusing on alloys is one of the R&D directions [5]. Thanks to its high catalytic ability in various reactions, platinum is the most

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studied metal and is used as the main metal of the great majority of bimetallic alloys. Many combinations exist and some choices are required. Wasmus and Küver [6] suggested that a clear-cut strategy was necessary in order to seek new catalysts and the best strategy for this search would be a combined approach of theoretical and fundamental electrochemical studies. The authors added that the knowledge of the oxidation mechanism was necessary to avoid a purely empirical approach.

Nørskov and co-workers [7–9] discussed how the calculation methods in close conjunction with the experiments could be used to develop concepts in order to describe and understand adsorptions and reactions on metallic surfaces. Interestingly, the authors emphasised on the variations in reactivity of transition metals in order to predict the effects of alloying. Following the suggestion of Wasmus and Küver [6], Nørskov and co-workers' studies [7–9] could then be used to try to find new bimetallic catalysts.

The present paper focuses on the anode electrocatalysts of three PEMFCs fed with liquid fuels, namely methanol, ethanol or formic acid. These three systems have been regarded because they are most studied and the three fuels are light carbon-based organic molecules. The main purpose is to discuss, on the basis of the Nørskov and co-workers' theoretical work [7–9], the best bimetallic anode electrocatalyst used for each system. It is also proposed a very brief review about fundamentals and the best anode electrocatalysts. Finally, the Nørskov and co-workers' theoretical study [7–9] is used to suggest, when possible, new bimetallic electrocatalysts.

2. Nørskov and co-workers' theoretical concepts

The work on “theoretical surface science and catalysis” of Nørskov and co-workers [7–9] can be a source of information for searching new anode electrocatalysts for fuel cells.

According to Nørskov and co-workers [7–9], the density functional calculations of adsorption and reactions at metal surfaces have reached a point that is sufficient for understanding bonding mechanisms. The chemisorption is indispensable for the reaction but an optimum have to be found for the metal-adsorbate bond strength. The authors focused on some simple concepts concerning the density of states of transition metals, which can be used to classify the reactivity of transition metal surfaces and to develop new and effective catalysts. The main conclusion is that, when considering variations in the reactivity of a particular metal or group of metals, the centre of the d-band (which is relative to the Fermi level) is strongly related to the stability of the atoms and the molecules on the surface as well as the energies of transition states for surface processes. The authors suggested two databases that are usable and useful for discussing the reactivity of bimetallic alloys. Alloying is a way of changing the reactivity of a given metal [10]. It can have different effects: (i) increase in the possible geometries of the adsorbates and reaction complexes; (ii) change in the electronic structures of the alloy in relation to those of the pure metallic surfaces of the alloy constituents; (iii) surface segregation of one element.

The first database (Table 1) deals with how alloying affects the reactivity. It provides an overview of the way the d-band cen-

Table 1
Shifts in d-band centres of surface impurities (A) and overlayers (B) relative to the clean metal values (bold)

	Fe	Co	Ni	Cu	Ru	Rh	Pd	Ag	Ir	Pt	Au
A											
Fe	-0.92	-0.05	-0.20	-0.13	-0.29	-0.54	-1.24	-0.83	-0.36	-1.09	-1.42
Co	0.01	-1.17	-0.28	-0.16	-0.24	-0.58	-1.37	-0.91	-0.36	-1.19	-1.56
Ni	0.09	0.19	-1.29	0.19	-0.14	-0.31	-0.97	-0.53	-0.14	-0.80	-1.13
Cu	0.56	0.60	0.27	-2.67	0.58	0.32	-0.64	-0.70	0.58	-0.33	-1.09
Ru	0.21	0.26	0.01	0.12	-1.41	-0.17	-0.82	-0.27	0.02	-0.62	-0.84
Rh	0.24	0.34	0.16	0.44	0.04	-1.73	-0.54	0.07	0.17	-0.35	-0.49
Pd	0.37	0.54	0.50	0.94	0.24	0.36	-1.83	0.59	0.53	0.19	0.17
Ag	0.72	0.84	0.67	0.47	0.84	0.86	0.14	-4.30	1.14	0.50	-0.15
Ir	0.21	0.27	0.05	0.21	0.09	-0.15	-0.73	-0.13	-2.11	-0.56	-0.74
Pt	0.33	0.48	0.40	0.72	0.14	0.23	-0.17	0.44	0.38	-2.25	-0.05
Au	0.63	0.77	0.63	0.55	0.70	0.75	0.17	0.21	0.98	0.46	-3.56
B											
Fe	-0.92	0.14	-0.04	-0.05	-0.73	-0.72	-1.32	-1.25	-0.95	-1.48	-2.19
Co	-0.01	-1.17	-0.20	-0.06	-0.70	-0.95	-1.65	-1.36	-1.09	-1.89	-2.39
Ni	0.96	0.11	-1.29	0.12	-0.63	-0.74	-1.32	-1.14	-0.86	-1.53	-2.10
Cu	0.25	0.38	0.18	-2.67	-0.22	-0.27	-1.04	-1.21	-0.32	-1.15	-1.96
Ru	0.30	0.37	0.29	0.30	-1.41	-0.12	-0.47	-0.40	-0.13	-0.61	-0.86
Rh	0.31	0.41	0.34	0.22	0.03	-1.73	-0.39	-0.08	0.03	-0.45	-0.57
Pd	0.36	0.54	0.54	0.80	-0.11	0.25	-1.83	0.15	0.31	0.04	-0.14
Ag	0.55	0.74	0.68	0.62	0.50	0.67	0.27	-4.30	0.80	0.37	-0.21
Ir	0.33	0.40	0.33	0.56	-0.01	-0.03	-0.42	-0.09	-2.11	-0.49	-0.59
Pt	0.35	0.53	0.54	0.78	0.12	0.24	0.02	0.19	0.29	-2.25	-0.08
Au	0.53	0.74	0.71	0.70	0.47	0.67	0.35	0.12	0.79	0.43	-3.56

The surfaces considered are the closest packed and the overlayer structures are pseudomorphic. All values are in eV and the elemental d-band centres are relative to the Fermi level. Adapted from Refs. [7–9].

Table 2
Compilation of calculated segregation energies on the closest packed surface of all binary combinations of transition metals

	3d								4d								5d							
	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Hf	Ta	W	Re	Os	Ir	Pt	Au
3d																								
Ti	n	A1	S1	S2	S2	S2	S3	S3	S2	n	A1	S1	S2	S2	S3	S3	S1	A1	A2	A1	n	S2	S3	S3
V	S2	n	A1	A2	A2	A1	S1	S2	S3	S2	A1	A2	A2	A1	S1	S3	S3	S1	A2	A2	A2	A2	A1	S2
Cr	S3	S1	n	S1	S2	S2	S3	S3	S3	S2	S2	S3	S3	S3	S3	S3	S2	S1	S1	S1	S3	S3	S3	
Mn	S3	S2	S1	n	S1	S1	S2	S3	S3	S3	S2	S2	S2	S3	S3	S3	S3	S2	S2	S2	S2	S2	S3	
Fe	S2	A1	A1	S1	n	S1	S2	S3	S3	S2	S1	A1	S1	S2	S3	S3	S2	A1	A2	A1	A2	A1	S1	
Co	S2	A1	A1	A1	n	n	S1	S2	S3	S2	n	A2	A1	S2	S3	S2	S1	A2	A3	A2	A2	S1	S2	
Ni	S1	A1	A1	n	A1	A1	n	S1	S3	S1	A1	A2	A1	S1	S2	S3	S3	n	A2	A2	A2	A2	A1	S1
Cu	n	A1	A1	A1	A1	A2	A1	n	S2	n	A1	A2	A1	A1	S1	S2	S2	A1	A2	A2	A2	A2	A1	n
4d																								
Zr	A1	n	S2	S2	S2	S2	S2	S3	n	A1	A1	n	S1	S2	S2	S3	A1	A2	A2	A1	n	S1	S2	
Nb	S1	A1	A2	A1	A1	A2	A1	S1	S2	n	A2	A2	A2	A1	S2	S2	A1	A2	A2	A3	A3	A3	A2	
Mo	S1	A1	n	S2	S2	S3	S3	S3	S3	S1	n	S1	S3	S3	S3	S3	n	A1	A1	S2	S1	S2	S3	S3
Tc	S3	S2	S1	S1	S1	n	S1	S2	S3	S3	S1	n	n	S1	S2	S3	S3	S2	A1	A1	A2	A1	S1	S3
Ru	S2	A1	A1	S2	S2	S2	S3	S3	S3	S2	A1	A1	n	S2	S3	S3	S3	S1	A1	A2	A1	A2	S1	S3
Rh	A1	A2	A2	S1	n	n	S1	S2	S2	A1	A2	A2	A2	n	S2	S3	S1	A2	A2	A3	A2	A1	S1	S3
Pd	A2	A3	A2	A2	A2	A1	A1	n	A2	A3	A3	A3	A3	A2	n	S1	A2	A3	A3	A3	A3	A3	A2	S1
Ag	A2	A2	A1	A1	A2	A2	A2	A1	A2	A2	A3	A2	A2	A2	A1	n	A2	A3	A3	A3	A3	A3	A2	n
5d																								
Hf	n	n	S2	S2	S2	S2	S3	S3	S1	A1	S1	S1	S2	S2	S3	S3	n	A1	A1	n	S1	S2	S3	S3
Ta	S2	n	A1	A1	A1	A1	S1	S2	S3	S1	A1	A2	A2	A1	S1	S2	S2	n	A2	A3	A3	A2	A1	S2
W	n	n	S1	S1	S2	S2	S2	S3	S3	S2	S1	S2	S3	S3	S3	S3	S3	S1	n	S1	S3	S3	S3	S3
Re	S3	S2	S1	S1	S1	S1	S2	S3	S3	S3	S2	S1	S1	S2	S2	S3	S3	S3	S1	n	n	S1	S2	S3
Os	S1	A1	A2	S1	S2	S2	S3	S3	S3	S2	A1	A1	S1	S2	S3	S3	S3	S1	A1	A1	n	S2	S3	S3
Ir	A1	A2	A2	A1	A1	A1	A1	S1	S2	A1	A2	A2	A1	S1	S2	S3	S1	A1	A2	A2	A2	n	S2	S3
Pt	A2	A3	A2	A2	A2	A2	A2	A2	A1	A3	A3	A3	A2	A2	n	S1	A2	A3	A3	A3	A3	A2	n	S2
Au	A2	A2	A2	A2	A2	A2	A2	A2	A1	A2	A2	A2	A2	A2	A1	n	A2	A3	A3	A3	A2	A2	A2	n

Adapted from Refs. [7–9]. S1, S2, S3: moderate, strong and very strong segregation, respectively; A1, A2, A3: moderate, strong and very strong antisegregation, respectively; n: no segregation.

tres change when a metal is alloyed with another. The database proposes the shifts in the d-band centres of metals in two-metal alloys. The alloys are combinations of some catalytically interesting materials, i.e. Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt and Au. This database can be used to get an idea about the possible means of modifying the electronic structures of metallic surfaces.

The second database (Table 2) is about the segregation phenomenon. The tendency of one metal to segregate to the surface of another metal largely controls the alloy surface composition. A compilation of the calculated segregation energies for all the binary combinations of transition metals is suggested.

Regarding the segregation phenomenon, it is also known that, for similar atomic sizes, the metal of the alloy having the lower heat of sublimation tends to segregate [11]. For similar heats of sublimation, it is the metal with the smallest atomic radius that tends to segregate [12]. Moreover, the metal having the larger Wigner-Seitz radius segregates [13] (the Wigner-Seitz radius is defined as the radius of a sphere of the same volume as the volume per particle). In fact, the driving force for the surface segregation is the reduction in the surface energy of the segregated alloy [14].

To better understand the relationship between the surface composition and the catalytic activity, it is very important to determine if surface segregation occurs for the bimetallic alloys.

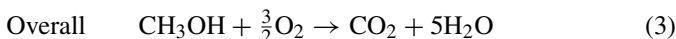
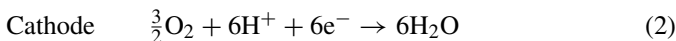
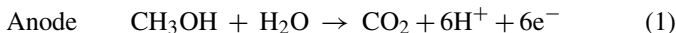
As a conclusion, Nørskov and co-workers [7–9] suggested that their databases may turn out to be useful in choosing interesting combinations of metals to investigate experimentally. Thereby, within the scope of the present paper, these databases will be used as theoretical tools in order to discuss the alloys tested through the literature and to predict, when possible, new combinations.

It is also important to recall that, in metallic catalysis, the change in reactivity is often explained in terms of electronic effect and/or geometric effect [10,15]. The key point in the electronic effect model lies in the interaction between the incomplete d-band of the metal surface sites with molecular orbitals of reactants and products. The electronic structure of the metals may be changed by alloying. If so, the bond strength of the adsorbed species and thereby their reactivity may change as well. The geometric effect, or ensemble effect, supposes that some reactions need more than one surface atom to proceed and that a specific arrangement between those atoms will even be required to generate the active sites.

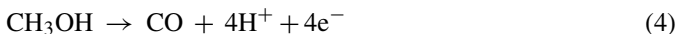
3. Multimetallic electrocatalyst for the direct methanol fuel cell

The direct methanol fuel cell (DMFC) is the most investigated liquid-feed fuel cell. As noticed in the introduction, the methanol has some interesting advantages and more particularly its direct

oxidation releases six electrons per molecule:



The overall reaction looks like a combustion reaction. The standard cell voltage is 1.21 V at 25 °C. In fact, the ideal anodic reaction is not completely reached as methanol is mainly decomposed into CO, which can further be oxidized into CO₂. The formations of CO and CO₂ are assumed occurring according to a dual path mechanism in the oxidation, one leading to CO (4) and another to CO₂ (1) [16]:



Other CO-like species are also formed during the adsorption phase, COH_{ads}, HCO_{ads}, HCOO_{ads}, and the principle by-products are formaldehyde and formic acid [17,18]. Some of the adsorbed species are not readily oxidizable and remain strongly adsorbed on the catalyst surface. Consequently, they prevent fresh methanol from adsorbing and undergoing further reaction. The methanol oxidation is a slow reaction that requires active multiple sites: the ones for adsorbing methanol and the others for donating OH species that are necessary for the desorption/oxidation of the adsorbed intermediates [19].

Platinum is the most active metal for the dissociative adsorption of methanol but it is readily poisoned by CO. Therefore, new electrocatalysts must be developed with the following objectives: resistance towards poisoning, increase of the reaction (3) rate and better activity towards CO₂ formation. A second metal that can provide oxygenated species at lower potentials for oxidative removal of adsorbed CO is needed [20]. According to Wasmus and Küver [6], it is virtually undisputed that Pt-Ru is better than Pt and there is a consensus about the fact that, for the methanol oxidation, Pt-Ru is the best material among the Pt-based bimetallic electrocatalysts [6,17–21].

These two metals, i.e. Pt and Ru, have close electronegativities (Fig. 1) and similar bulk Wigner-Seitz radii (Fig. 2). Pt when alloyed with Ru strongly segregates while Ru strongly antise segregates (Table 2), thereby a Ru site should be surrounded with some Pt sites, what is in agreement with the three to five Pt atoms necessary to activate the adsorption of methanol and the single Ru atom necessary to activate water [5]. Moreover, the Pt electronic structure should be changed by the presence of neighbouring Ru. According to Table 1, the Pt d-band centre shifts down when Pt is alloyed with Ru, what suggests weaker Pt-adsorbate bonds, while the Ru d-band centre slightly shifts up. In other words, when Pt and Ru are alloyed, the adsorption of adsorbates is weaker on the Pt sites and stronger on the Ru sites. These tendencies may explain the enhanced activity of Pt-Ru, which is attributed to both bifunctional mechanism and electronic effect, where the bifunctional mechanism involves the adsorption of OH species on Ru atoms thereby promoting the oxidation of CO to CO₂ [22,23]. In this way, the Pt poisoning by the CO-like species would be decreased because these species would more weakly adsorb on Pt and Ru would provide the nec-

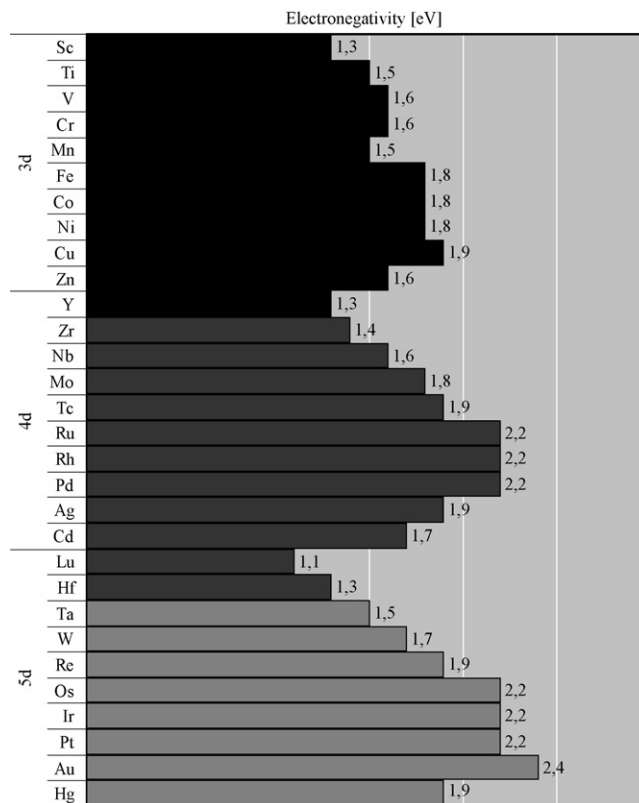


Fig. 1. Electronegativity [eV] of the transition metals.

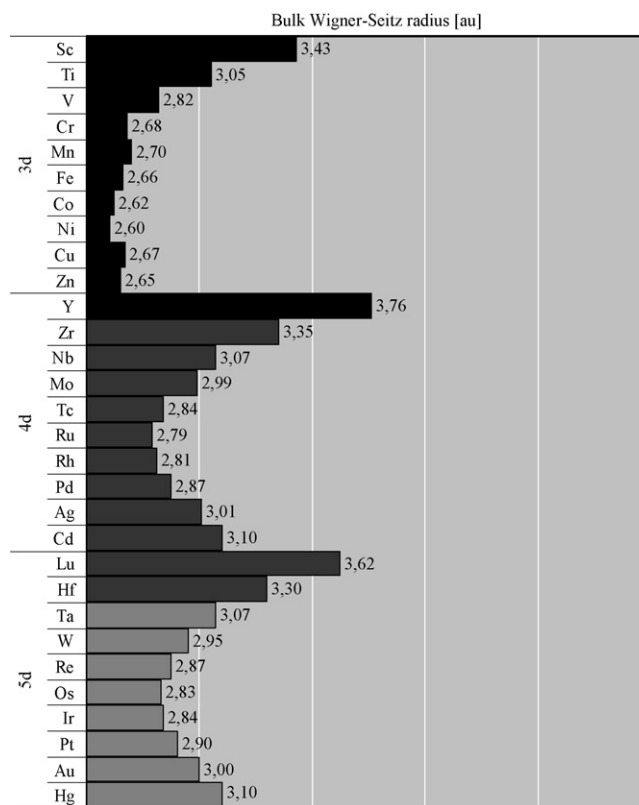


Fig. 2. Bulk Wigner-Seitz radius [a.u.] of the transition metals. Adapted from Ref. [8].

Table 3

Possible occurrence of segregation and possible shift in d-band centre for the elements of the trimetallic Pt-Ru-M alloy [5] with metals (M) as Mo, W, Co, Fe, Ni, Cu, Sn and Au

	Pt-Ru-M alloys							
	Pt-Ru-Mo > Pt-Ru-W > Pt-Ru-Co > Pt-Ru-Fe > Pt-Ru-Ni > Pt-Ru-Cu > Pt-Ru > Pt-Ru-Sn > Pt-Ru-Au							
	Mo	W	Co	Fe	Ni	Cu	Sn	Au
M segregation in relation to Pt ^a	A3	A3	A2	A2	A2	A2	S ^b	S2
M segregation in relation to Ru ^a	A1	A1	S2	S2	S3	S3	S ^b	S3
Pt d-band centre [eV] ^a	n.i.	n.i.	Down shift	Down shift	Down shift	Down shift	n.i.	Up shift
Ru d-band centre [eV] ^a	n.i.	n.i.	Down shift	Down shift	Down shift	Up shift	n.i.	Up shift

S1, S2, S3: moderate, strong and very strong segregation, respectively; A1, A2, A3: moderate, strong and very strong antisegregation, respectively; n: no segregation. n.i.: not informed in Refs. [7–9].

^a Adapted from Refs. [7–9].

^b Deduced from the metals heat of sublimation [35].

essary OH species, which would permanently be available on the Ru surface sites, more strongly adsorbing the OH species.

Elements as alternative to Ru were investigated. Antolini et al. [19] worked on Pt₃Co₁ and Pt₃Ni₁ (atomic ratio 3:1). The authors chose Co and Ni since their presence lowered the electronic binding energy in Pt and so promoted the C–H cleavage reaction at low potentials and, moreover, they provided OH species necessary for the CO oxidation. The performances of fuel cells with Pt₃Co₁ or Pt₃Ni₁ as anode catalysts were slightly worse than that of the fuel cell with Pt. The performance of Pt₃Co₁ was slightly better than that of Pt₃Ni₁. These two metals, i.e. Co and Ni, have similar electronegativities (Fig. 1) and bulk Wigner-Seitz radii (Fig. 2). According to Table 2, Pt when alloyed with Co strongly segregates and Pt when alloyed with Ni moderately segregates, as already reported [24,25]. For both Pt-Co and Pt-Ni, the Pt d-band centre shifts down. The d-band centres of Co and Ni shift up when they are alloyed with Pt. This analysis of the surface modifications suggests the following remarks: compared with Pt-Ru, (i) the adsorption of OH species on the Co or Ni sites should be weaker; (ii) the lower segregation of Pt in either Pt-Co or Pt-Ni is an indication of a higher dilution of Pt and so a decrease in the number of Pt surface sites. Therefore, Pt-Ru should be a better catalyst than both Pt-Co and Pt-Ni, and as the Pt segregation is more severe with Co, Pt-Co should be a better catalyst than Pt-Ni with a larger number of Pt surface sites. However, as underlined by Antolini et al. [17], conflicting results regarding the Pt-Co and Pt-Ni alloys were reported in the literature. Interestingly, the authors showed that the methanol oxidation activity on Pt-Ni and Pt-Co was improved or unchanged or decreased in relation to pure Pt. It was observed an opposite effect of the Co/Ni presence in going from low contents (negative effect on the methanol oxidation) to high contents (positive effect) and the decreased activity in the presence of low Co/Ni contents was ascribed to the dilution of Pt, hindering the methanol adsorption, while the positive effect was related to several reasons, namely the electronic effect, an enhancing of the CO oxidation and the presence of oxide species [17]. This study unfortunately shows the limitations of the theoretical understanding of the catalysts behaviours but it fortunately stresses on the essential side of the experiments.

Choi et al. [26] observed that the current density produced by methanol oxidation over Pt₂-Rh₁ (atomic ratio 2:1) was larger

than that over pure Pt but lower than that over Pt-Ru. The authors concluded that the enhanced activity of Pt₂-Rh₁ was mainly due to an intrinsic improvement in catalytic activity and not to an improvement in CO oxidation. Ru and Rh display similar electronegativities and bulk Wigner-Seitz radii (Figs. 1 and 2). Pt moderately segregates when alloyed with Rh while it very strongly segregates when alloyed with Ru. The Pt d-band centre shifts down when alloyed with both though the down shift is more important with Ru. These reflections suggest that Pt-Ru should be better with higher surface concentration of Pt sites and lower strength of the adsorption of CO-like species over the Pt sites.

More recently, Choi et al. [27] reported that the Pt-Au alloy and pure Pt showed almost the same activity. Au itself was inactive for methanol oxidation and was not helpful for removing CO_{ads} on the Pt surface. In fact, when alloyed with Au, Pt strongly antisegregates (Table 2). The surface concentration in Pt sites is then reduced. Moreover, Au has one of the lowest d-band centres and the presence of Pt shifts down it, what suggests very poor abilities for the adsorption of OH species. The Pt d-band centre shifts up when alloyed with Au and thereby the adsorption of CO-like species becomes stronger, what favours the Pt sites poisoning. Consequently, Au is not interesting for the preparation of active Pt-based bimetallic alloys devoted to methanol oxidation.

Pt-Ru-based trimetallic electrocatalysts were envisaged as well [5]. The addition of a third element, i.e. Au, Co, Cu, Fe, Mo, Ni, Sn and W, gives promising results. The following classification enabled to note that Mo, W, Co, Fe and Ni improved the Pt-Ru activity towards the oxidation of methanol, the best promoter being Mo: Pt-Ru-Mo > Pt-Ru-W > Pt-Ru-Co > Pt-Ru-Fe > Pt-Ru-Ni > Pt-Ru-Cu > Pt-Ru > Pt-Ru-Sn > Pt-Ru-Au. Even if the concepts of Nørskov and co-workers [7–9] do not consider the alloys with three metals, it could be tried out proposing few trends regarding the segregation and the d-band centres variations. Table 3 proposes the possible occurrence of the segregation and the shifts in d-band centres for the different metals, i.e. Pt, Ru, Mo, W, Co, Fe, Ni, Cu and Au. The analysis of the data given by Table 2 suggests that the best trimetallic catalysts are the ones for which the third metal M antisegregates while both Pt and Ru segregate. Furthermore, it seems that the d-band centres of Pt and Ru should shift down. The trimetallic material

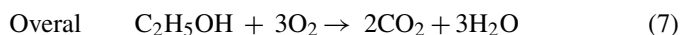
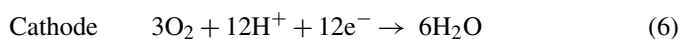
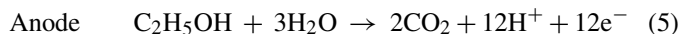
for which the d-band centres of Pt and Ru shift up is the worst alloy. Unfortunately, these types of data are not available for Mo, W and Sn what would have been useful to completely validate such observations. Consequently, the improvement of the Pt-Ru alloys would require a third metal with which Pt and Ru would segregate and their d-band centres would shift down.

All of the previous observations could be used as criteria to select, from Tables 1 and 2, bimetallic catalysts that could be active for the methanol oxidation. The first criterion could be the d-band centre shift. It should be close to that of Pt and Ru when alloyed together, i.e. about -2.9 and about -1.3 eV, respectively. Thereby, the analysis of Table 1 provides Pd-Ni. The second criterion could be the segregation. Hence, Table 2 confirms Pd-Ni as Pd has a tendency to strongly segregate (like Pt) while Ni moderately antisegregates (like Ru). Therefore, the Pd-Ni alloy might provide an activity similar to that of Pt-Ru. Nevertheless, for the methanol oxidation, as it is remarked by a large number of investigations, the best current way to improve the anode electrocatalyst would be the addition of a third metal to Pt-Ru [5].

Many investigations about DMFC have more or less regarded all the mono- and bimetallic electrocatalysts displaying catalytic abilities towards methanol oxidation. It seems then that the remaining tracks to follow are the trimetallic alloys and especially the Pt-Ru-based ones.

4. Multimetallic electrocatalyst for the direct ethanol fuel cell

Ethanol is an alternative fuel to methanol because it has the advantage of not having the drawbacks of methanol. The direct ethanol fuel cell (DEFC) is based on the oxidation of ethanol, involving 12 electrons (cell electromotive force of 1.15 V):



Like the DMFC, the overall reaction looks like a combustion reaction. The principle by-products are acetaldehyde and acetic acid [28,29]. The main drawbacks are the slow kinetics and the catalyst poisoning by CO-like intermediates at low temperatures [28,30]. The ethanol oxidation is more complicated than the methanol oxidation because the breaking of the C–C bond to obtain its complete oxidation is necessary. Therefore, the anode electrocatalyst for DEFC must cleave the C–C bond at low temperatures and oxidize the CO-like intermediates.

The most common anode electrocatalyst is Pt but it is rapidly poisoned by strongly adsorbed intermediates like, e.g. CO (resulting from the dissociative chemisorption of ethanol) [5]. The main objective is then the improvement of the anodic performances and there is a consensus about the utilization of multifunctional electrocatalysts [31] and more precisely of Pt-based bimetallic materials [29]. Besides, Lamy et al. [31] added that the only possibility to overcome the catalyst poisoning was to modify the electrode surface in such a way to increase its

coverage in adsorbed OH coming from water. The OH species are necessary to oxidize the CO-like species coming from the dissociation of ethanol into CO_2 .

Pt-Sn shows the best results [5,29–34]. It greatly enhances the oxidation of CO to a larger extent than Pt-Ru, the maximum power obtained with Pt-Sn being three times the value obtained with Pt [31]. Sn (or its oxides) [33] supplies OH species for the oxidative removal of CO-like species strongly adsorbed on adjacent Pt sites. Pt-Sn promotes the cleavage of C–C bond and improves the removal of CO_{ads} species [30]. Unfortunately, the Nørskov and co-workers' database [7–9] do not include Sn. By taking into account the heats of sublimation of Pt and Sn (116 and 60 kcal mol $^{-1}$, respectively [35]), Sn would segregate and Pt would antisegregate.

Zhou et al. [32] reported that Sn, Ru, Pd and W could enhance the ethanol oxidation activity over Pt in the following order: Pt-Sn > Pt-Ru > Pt-W > Pt-Pd > Pt. Better results with Pt-Ru in relation to Pt were also published by Liu et al. [36]. Furthermore, Song et al. [34] remarked that Pt-Sn could oxidize ethanol to a deeper extent than Pt-Ru. The segregation phenomena are similar for Pt-Ru and Pt-W: Pt strongly segregates and W strongly antisegregates (Table 2). Unfortunately, no information about the d-band centre is given for W (Table 1). If one assumes that the behaviour of W is close to that of Ir, the d-band centre of Pt might shift down but at a degree inferior to that occurring when alloyed with Ru. Regarding the Pt-Pd alloy, no segregation should occur (Table 2), but Ponec [37] and Bertolini [25] reported a Pd surface enrichment for Pt-Pd alloys. The Pt d-band centre shifts up (if regarded as impurities) or remains unchanged (if regarded as overlayer) while the Pd d-band centre shifts down (if regarded as impurities) or remains unchanged (if regarded as overlayer). Hence, on the basis of the observations done in the section devoted to the DMFC, a lower activity for the Pt-Pd catalyst in relation to Pt-Ru was expectable.

With Pt-Sn, the poisoning by CO is greatly reduced and a significant enhancement of the electrode activity takes place. However, the oxidation of ethanol is incomplete and C_2 products are formed [31,34]. Léger et al. [29] suggested that two main routes existed for the overall mechanism of the ethanol oxidation over Pt-Sn. The first was the formation of adsorbed CO. The second involved the formation of C_2 -species, e.g. $\text{CH}_3\text{CHO}_{\text{ads}}$ (acetyl), which could lead to the formations of acetaldehyde and acetic acid as final products.

For Song et al. [34], the development of a novel catalyst or the addition of a third element to Pt-Sn or Pt-Ru is crucial. It will be expected from these new catalysts to be more active towards dehydrogenation, C–O and C–C bond cleavages during the ethanol oxidation. Moreover, it is to notice that the bond breakings take place in a narrow temperature range, characteristic of the adsorbate–adsorbent system [10] and that is why besides the research of new active alloys, the oxidation temperature should be optimised to get the C–C bond breaking.

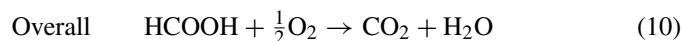
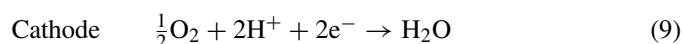
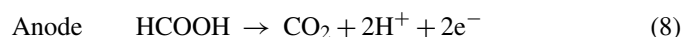
It is possible to inventory the bimetallic alloys that may be assessed. The analysis of Tables 1 and 2 suggest Pd-Ni. However, it is likely that this catalyst would not be as active as Pt-Ru or Pt-Sn towards the C–C bond cleavage because Pd is not as active as Pt towards the C–C bond activation [38]. Indeed, Ponec

[38] reported that the metals Pt and Pd were very inactive in hydrogenolysis while Ru, Co and Ni were active metals for this reaction. However, Ni could be seen as the active metal and Pd as the promoter. Such Pd-Ni alloy might have a certain activity but experiments are necessary in this case. Consequently, it seems that the best choice in the development of new catalysts for the DEFC is very likely the addition of a third element to either Pt-Sn or Pt-Ru. At this stage, it is difficult to propose from the theoretical tools any third metal for Pt-Sn because data lacks about Sn [7–9]. Regarding Pt-Ru, it is likely that the same third elements than those used for the DMFC would provide good results. That is why, Pd, Ag and Au should be avoided because Pt in their presence is diluted on the catalyst surface. The segregation of Ru is favoured with V, Cr, Mo, Tc, W, Re and Os. Unfortunately, the absences of V, Cr, Mo, Tc, Re and Os in Table 1 do not enable any discussion about the shifts in the d-band centres of Pt and Ru, but it is possible that down shifts of these values would be benefit to the activity of the trimetallic alloys.

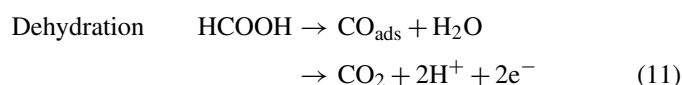
As a conclusion, it seems that the investigations areas regarding the DEFC anode electrocatalyst fall on the trimetallic alloys.

5. Multimetallic electrocatalyst for the direct formic acid fuel cell

The direct formic acid fuel cell (DFAFC) has a high theoretical open circuit voltage of 1.45 V. Its direct oxidation releases two electrons per molecule:



The mechanism of the formic acid oxidation on Pt follows the so-called dual pathways that are dehydrogenation (8) and dehydration (11) [39,40]. According to the dehydrogenation path or direct path, formic acid is directly dehydrogenated into CO₂ via one or more active intermediates. According to the dehydration path or CO path, formic acid is dehydrated into CO, which poisons the electrode or is further oxidized to produce CO₂:



Li and Hsing [41] investigated Pt-Pd and observed that Pd not only exhibited activity for formic acid oxidation but also provided a synergetic effect to Pt, which oriented Pt-Pd in favour of formic acid oxidation via the direct path. Rice et al. [42] also studied Pt-Pd. They reported that Pt-Pd had higher overall cell efficiencies than both Pt and Pt-Ru: at 0.5 V, there was about an 80% increase in activity over that of both Pt and Pt-Ru; at lower potentials, the Pt and Pt-Pd performances were similar; the Pt-Ru catalyst performed best at potentials below 0.4 V. From Table 2, one can remark that Pd and Pt do not segregate. The surface of Pt-Pd should be occupied by these two metals in the proportions of the alloy. Pt and Pd are very similar elements in terms of their electronegativities (Fig. 1) and bulk Wigner-Seitz

radii (Fig. 2). Furthermore, Pd is a metal known for its ability to catalyse the oxidation of CO and of hydrocarbons [10]. In this case, i.e. Pt-Pd, Pd does likely not act as an OH source because they are not required for the direct oxidation of formic acid, but Pd likely influences the surface reactions by geometric effect. It is possible to explain the best activity of Pt-Ru at the lowest potentials by the ability of Ru to provide OH species necessary for the oxidation of the CO-like species that poison the Pt surface. The role of Pd would be quite different from that of Ru. Pd would modify the Pt environment and so the Pt reactivity, while Ru would act as a source of OH species.

Marković and Ross [21] underlined that the formic acid oxidation was a reaction where the ensemble effect was very important. They observed a significant enhancement of the activity of the Pt surface by modification with either Ru or Sn and reported that the very strong ensemble effects observed with Ru- and Sn-modified surfaces meant that it was necessary to control the surface composition when exploring new systems. Pt-Ru are reported as the best electrocatalyst and the enhanced activity of Pt-Ru is attributed to the bifunctional mechanism that involves the adsorption of OH species on Ru thereby promoting the oxidation of CO to CO₂ [22,23,27,42]. In fact, as observed for both DMFC and DEFC, the best choice to hinder the Pt poisoning by the CO-like species is the presence of few Ru atoms at the surface, which provide the OH species required for the CO-like species oxidation and so contribute to the “freedom” of the Pt sites.

Choi et al. [27] compared Pt-Au and Pt-Ru and observed a better oxidation activity for Pt-Au. The maximum power densities for the corresponding DFAFC were 94 and 74 mW cm⁻², respectively. The authors suggested that the enhancement of formic acid oxidation was likely due to the so-called third-body effect, which meant that the addition of a second element (third body) to Pt reduced the number of adsorption sites for CO due to geometrical hindrance and therefore the surface was poisoned by the CO_{ads} to a lesser extent than the pure Pt surface. This effect may also explain the better formic acid activity of Pt-Pd previously described. In presence of Au, Pt strongly antisegregates (Table 2) and its d-band centre shifts up, while the Au d-band centre remains quite constant (Table 1). These observations are in agreement with the explanation provided by Choi et al. [27]: the segregation of Au reduces the number of adsorption sites for CO due to geometrical hindrance and the formic acid oxidation increases because the Pt poisoning is partly avoided. Ponc [37] reported that the dilution of an active metal as Pt in an inactive matrix as Au took place with the consequence that the big ensembles of the active metal sites disappeared or at least were dramatically reduced in their number.

It is possible that some promising Pt-based bimetallic systems have been missed and it is necessary to search for new bi- or trimetallic electrocatalysts [21]. By using the analysis previously done for Pt-Pd and Pt-Au, it stands out that the surface Pt should dilute and that the Pt d-band centre should shift up, i.e. that the adsorption of adsorbates should be stronger. In fact, the choices are limited (Tables 1 and 2). With V, Cu, Nb, Pd, Ag, Ta and Au, Pt antisegregates. With Pd, Ag and Au, the Pt d-band centre shifts up. As Pt-Pd [41,42] and Pt-Au [27] have

already been evaluated and have showed promising results, the single choice that remains is Pt-Ag, which might be a promising catalyst, maybe similar to Pt-Au.

The trimetallic alloys are an area to explore for new formic acid oxidation electrocatalysts. To begin, combinations of Pt, Pd, Ag and Au, with Pt as the permanent feature, may be envisaged.

6. Conclusions

Focusing on the anode electrocatalysts of three direct liquid-feed fuel cells, the present paper mainly attempts to interpret the alloys catalytic behaviours from the databases taken from Nørskov and co-workers' theoretical work [7–9]. These databases are related to the d-band centre shift and the segregation phenomenon of transition metals, which can occur when two metals are alloyed.

For the methanol oxidation in DMFC, the best current catalyst is Pt-Ru, for which the Pt d-band centre is shifted down and Pt is strongly segregated. These two modifications enable to interpret its improved catalytic activity in relation to pure Pt. The down shift in the Pt d-band centre leads to weaker adsorptions of CO-like species and the strong segregation of Pt dilutes Ru that is a source of OH species necessary to oxidized the CO-like species adsorbed on Pt. Hence, Pt-Ru is more active and the poisoning threat of CO-like species is considerably reduced.

For the ethanol oxidation in DEFC, the electrocatalysts must be active towards dehydrogenation, C–O and C–C bond cleavages. Pt-Sn shows the best results. It promotes the cleavage of the C–C bond and improves the removal of the CO_{ads} species. As Sn is unfortunately an element for which no data are available through the Nørskov and co-workers' databases, no interpretation can be given.

For the formic acid oxidation in DFAFC, Pt-Pd is a promising electrocatalyst. Pd and Pt do not segregate and the surface of Pt-Pd is likely occupied by these two metals in the proportions of the alloy. The third-body effect may explain its better activity in relation to Pt. From the theoretical analysis of the databases and the trends provided by the alloys already investigated, it is possible to predict that Pt-Ag might be a good candidate for the formic acid oxidation.

For all the direct liquid-feed fuel cells regarded in the present paper, it seems that the future tracks for searching more active and/or new catalysts are the trimetallic alloys.

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