



Review

Alloy vs. intermetallic compounds: Effect of the ordering on the electrocatalytic activity for oxygen reduction and the stability of low temperature fuel cell catalysts



Ermete Antolini

Scuola di Scienza dei Materiali, Via 25 aprile 22, 16016 Cogoletto, Genova, Italy

ARTICLE INFO

Article history:

Received 30 March 2017

Received in revised form 23 May 2017

Accepted 27 May 2017

Available online 30 May 2017

Keywords:

Polymer electrolyte membrane fuel cell

Oxygen reduction

Catalyst

Ordering

Stability

ABSTRACT

The application of intermetallic compounds in heterogeneous catalysis had a significant boost during the last decade. Notwithstanding the advantages related to the use of intermetallics in catalysis, random alloys, more easy to prepare, are commonly used as catalysts in low temperature polymer electrolyte membrane fuel cells (LT-PEMFC). In various papers, however, the use of Pt- and Pd-based intermetallics in LT-PEMFCs is reported. In this work an overview of the effect of the crystal structure ordering on the activity for oxygen reduction and stability of fuel cell catalysts is discussed, by comparing ordered and disordered structures with the same A/M (A = Pt, Pd; M = first row transition metal) atomic ratio and ordered structures with different A content.

© 2017 Elsevier B.V. All rights reserved.

Contents

1. Introduction	202
2. Structure of Pt- and Pd-based binary and ternary alloys and intermetallics	202
2.1. Binary catalysts	202
2.1.1. Crystal structure	202
2.1.2. Surface composition	203
2.2. Ternary catalysts	204
2.2.1. Crystal structure	204
2.2.2. Surface composition	204
3. Activity and stability of binary A-M (A = Pt, Pd; M = first row transition metal) alloys and intermetallics for the oxygen reduction reaction	204
3.1. Fcc Pt ₃ M (M = Cr, Fe, Co), PtM ₃ (M = Co, Cu) and Pd ₃ Fe alloys and intermetallics	205
3.1.1. Intrinsic ordering effect on the ORR activity	205
3.1.2. Stability of ordered catalysts	206
3.2. Pt ₁ M ₁ (M = Fe, Co, Ni) and Pd ₁ Cu ₁ alloys and intermetallics: disordered fcc to ordered fct or bcc phase transition and ordering increase in the fct crystal structure	207
3.2.1. Intrinsic ordering effect on the ORR activity	208
3.2.2. Stability of ordered catalysts	208
4. Ordered ternary catalysts for the oxygen reduction reaction: comparison with the corresponding disordered ternary and ordered binary catalysts	209
5. Comparison of ordered fcc Pt ₃ M and Pt ₃ Fe _{0.5} M _{0.5} catalysts with ordered fct PtM and PtFe _{0.5} M _{0.5} catalysts: effect of crystal structure and Pt content	209
6. Conclusions	211
References	211

E-mail address: ermantol@libero.it<http://dx.doi.org/10.1016/j.apcatb.2017.05.081>

0926-3373/© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Low temperature acidic fuel cells, fuelled with hydrogen or low molecular weight alcohols consist of an anode, to which the fuel is supplied, a cathode to which oxygen (or air) is supplied, and a polymer electrolyte membrane that permits the flow of protons from anode to cathode [1,2].

Platinum has the highest catalytic activity for oxygen reduction of any of the pure metals, thus unsupported and carbon supported platinum nanoparticles are commonly used as fuel cell electrocatalysts. The oxygen reduction reaction (ORR) electrocatalysis mainly depends on the interplay of electronic and geometric parameters, controlling the adsorption of oxygenated species [3]. Theoretical and experimental studies on the ORR have indicated that Pt–Pt bond compression results in d-band down-shift, weakening the bonding between Pt and oxygenated species and increasing the catalytic activity for the ORR [4,5]. For the ORR intermediates O and OH, this occurs by a simple electron interaction, where the adsorbate valence p-level forms bonding and antibonding states with the metal d-band. [6]. Population of any antibonding state will lead to Pauli repulsion, and the bond strength will thereby be weakened. A downward shift of the d-band will pull more of the antibonding states below the Fermi level, resulting in increasing occupation and weaker adsorbate bonding.

The high cost of platinum and kinetic limitations of the ORR, as well as the low alcohol tolerance when Pt is used as a cathode catalyst in direct alcohol fuel cells, are a major problem for the commercialization of low-temperature fuel cells. So the research focused on the development of cathode catalysts more active, more alcohol-resistant and less expensive than Pt alone, such as binary and ternary Pt-based [7,8] and Pd-based [9] catalysts. The suitability of binary and ternary Pt- and Pd-based catalysts as fuel cell cathode catalysts is mainly based on the fundamental relationship between the electronic surface structure and the ORR activity [10]. Depending on the center of the d-band vs. the Fermi level, a direction for development of suitable fuel cell catalysts was traced: highly active ORR catalysts will be obtained by the downshift of the d-band center vs. pure Pt, that is, by the weaker interaction of the oxygenated species with the surface [11]. Pt–M and Pt–M–M' (M, M' = first row transition metals) showed higher ORR activities than pure Pt [12,13], retained or enhanced even after removal of the transition metal from the catalyst surface and formation of a Pt rich shell by either naturally under operating conditions or intentionally selective leaching of the non-noble transition metal, due to the electronic (ligand effect) and geometric (strain effect) influence of the alloying element inside the core [14,15].

There are two major types of materials formed by two or more metallic elements, that is, alloys and intermetallics. Alloys, also referred as solid solutions, are random mixtures of metals, in which the elemental crystal structure of one of the constituent elements is adopted. Intermetallics are compounds with a defined stoichiometry and crystal structure, with specific sites assigned for the atoms of each constituent element. In intermetallics the position of two (or more) types of atoms is determined, not random. Such ordering differentiates the intermetallic compound from a “common” alloy. Intermetallics display special magnetic, superconducting and chemical properties, due to their strong internal order and mixed (metallic and covalent/ionic) bonding, which are not present in alloys. Alloys have less negative free energy of formation than intermetallics, resulting in a lower thermal stability, and leading to a surface rearrangement and phase separation. Moreover, random site occupancy of alloys limits the availability of catalyst active sites only to certain regions. Conversely, the regular structure of intermetallics would ensure homogeneity of the active sites.

Recently, the use of intermetallics in various chemical transformations, such as hydrogenation/dehydrogenation, oxidation, and

steam reforming, and their advantages over alloys has been surveyed [16,17]. Notwithstanding the advantages related to the use of intermetallics in catalysis, random alloys, more easy to prepare, are commonly used as catalysts in low temperature fuel cells (LT-FCs). In various papers, however, the use of Pt- and Pd-based intermetallics in LT-FCs is reported. Intermetallic compounds can be promising for their use as ORR fuel cell catalysts for two main reasons: 1) unlikely random site occupancy of alloys, in intermetallics the ‘good’ sites for the ORR are available in whole catalyst surface, and 2) they are more stable thermodynamically and are likely to be less susceptible towards surface rearrangement and phase separation under fuel cell operating conditions than random alloys. In this review the effect of the crystal structure ordering on the ORR activity and stability of fuel cell catalysts is discussed, by comparing ordered (O) and disordered (D) structures with the same A/M (A = Pt, Pd; M = first row transition metal) atomic ratio and ordered structures with different A content.

2. Structure of Pt- and Pd-based binary and ternary alloys and intermetallics

2.1. Binary catalysts

2.1.1. Crystal structure

Generally, Pt–M (M = first row transition metal) compounds present four main crystal structures, that is, a disordered Pt_{1-x}M_x solid solution, and the ordered intermetallic Pt₃M, PtM and PtM₃ intermetallics. The chemically disordered Pt_{1-x}M_x (x = 0–1) alloy has a face-centered cubic (fcc) structure (A1 phase, space group: Fm-3m), in which the Pt and M atoms are randomly distributed in all (0,0,0), (1/2,1/2,0), (1/2,0,1/2) and (0,1/2,1/2) crystallographic sites. Pt_{1-x}M_x alloys order at concentrations x = 1/4 and 3/4. In the ordered fcc Pt₃M structure M atoms occupy the eight corner positions and Pt atoms occupy six-face centered positions in the cube. The structures of Pt₃M and PtM₃ are both L1₂, space group: Pm-3m, where the roles of Pt and M are interchanged. Unlike the fcc structure, in the ordered face-centered tetragonal (fct) PtM structure (L1₀ phase, space group: P4/mmm) the M and Pt atoms form alternating layers within the crystal lattice, where Pt is in (0,0,0) and (1/2,1/2,0) sites, and M is in (1/2,0,1/2) and (0,1/2,1/2) sites. The fct structure breaks the cubic symmetry of the fcc structure by altering the length of one of the sides. As an example, the crystal structures of the disordered Pt_{1-x}Fe_x solid solution and the fcc Pt₃Fe and fct PtFe ordered phases are shown in Fig. 1 [18]. The fct structure, however, can present a certain degree of disorder, when antisites or antiphases are present. An antisite is formed when some M occupy the (0,0,0) and (1/2,1/2,0) sites and some Pt occupy the (1/2,0,1/2) and (0,1/2,1/2) sites. Vacancies are the other punctual defects present in these intermetallics. If the vacancy concentration is different on both sublattices, a stoichiometry departure will also be induced [19]. Punctual defects in the L1₀ structure (antisites and vacancies of both species) are shown in Fig. 2. Antiphase domain boundaries (APBs) are the most common type of extended defects unique to chemically ordered alloys. For example, the unit cell of ordered PtCo with the L1₀ structure type is made up of planes of all cobalt and platinum alternating along (002). A scheme of this structure type is shown in Fig. 3a [20] and a representation of the alternate stacking along the c-axis is given in Fig. 3b. The formation of a long-period antiphase structure from L1₀ is shown schematically in Fig. 3c. Halfway along the a₁-axis of the cell, the stacking sequence changes in that planes of all cobalt become all platinum and vice versa. Thus, the structure is divided into domains with adjacent domains being antiphase. The antisite defects, vacancy difference and antiphases are responsible in the stoichiometric alloys for the departure of the long-range order parameter from its maxi-

Download English Version:

<https://daneshyari.com/en/article/6453937>

Download Persian Version:

<https://daneshyari.com/article/6453937>

[Daneshyari.com](https://daneshyari.com)