

CO adsorption in Pd_xCo_yX_z (X = Au, Mo, Ni) tertiary alloy nanocatalysts for PEM fuel cells—a theoretical analysis

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SUMMARY

Application of tertiary alloy nanoparticles is becoming more important, however, the local structure of such alloyed particles, which is critical for tailoring their properties, is not yet very clearly understood. In this study, we present detailed theoretical analysis on the atomistic structure and CO adsorption in Pd₇₀Co₂₀X₁₀ (X = Au, Mo, Ni) tertiary composite alloys for their application in fuel cells toward oxygen reduction reaction (ORR). Basic structure and the most stable configurations for all the three composites are determined. Quantum mechanical approaches and classic molecular dynamics methods are applied to model the structure and to determine the lowest energy configurations. Our theoretical results agree well with the experimental results of XRD patterns. Considering those structures as the base, simulations were performed to determine the magnitude of CO poisoning. The results obtained by *ab-initio* calculations allow us to estimate the CO-tolerance that these catalysts might have, along with those obtained for Pd-Co-Ni (70:20:10 atom %) tertiary alloy, and compared with commercial Pt (1 1 0) catalyst. From these results, a comparison has been made to show different CO adsorption strengths. This is the first step to fabricate an efficient engineering design that allows us to obtain high-performance, low-cost nanostructured catalysts. Copyright © 2010 John Wiley & Sons, Ltd.

KEY WORDS

tertiary alloy; PEM fuel cells; CO adsorption; nanostructured catalysts

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1. INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are promising power sources for transportation, portable, and stationary applications. There is a decent review of the different flow field designs employed by stack developers and academic researchers, and a fairly expansive discussion of membrane electrolyte based on Nafion® material developed by DuPont de Nemours. However, the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode and high cost of

platinum-based noble metal electrocatalysts are two major challenges that impede the commercialization of PEMFCs. From previous reports [1–5], it can be understood that platinum alloys have shown higher electrocatalytic activities compared to other catalysts. Pt supported on carbon black is widely used as the electrocatalyst for ORR in PEMFC due to its high catalytic activity and an excellent chemical stability in the fuel cell environment [6]. Particularly difficult problem is the large over-potential of 0.3 to 0.4 V in the initial part of the polarization curves, which is the

source of declination in fuel cell's efficiency. This loss was partly attributed to the inhibition of O₂ reduction caused by OH⁻ adsorption on Pt in the potential region of 0.75 to 1 V. These challenges have created enormous interest in the search for less expensive, more efficient electrocatalysts as well as in lowering the catalyst loading [6–9]. Extensive investigations have been conducted to find alternative electrocatalysts that are more active and less expensive than the benchmark Pt/C catalysts. Recent studies have shown that most of the Pt alloy electrocatalysts are not stable in PEMFC operating conditions [10,11]. In addition to it, the high cost of Pt has led the researchers around the world to search for alternative catalysts. Some important reports available on alternative catalysts are non-platinum-based metal combinations, [12,13] metal oxides, [14,15] carbides, [16] chalcogenides, [17] enzymes, [18,19] inorganic and organometallic complexes, [20,21] and porphyrins. These catalysts are investigated over the years for ORR, but they generally exhibit lower catalytic activity than Pt and get poisoned easily. Probable solution to overcome the poisoning effects in fuel cell is to use alloyed catalysts, such as Pt/Ru, Pt/Mo, Pt/Ru/Mo, Pt/Sn, Pt/Ru/WO₃, etc. [22–25]. A carbon-supported Pd-based PdPt catalyst with a Pd:Pt atomic ratio of 19:1 was synthesized and applied to a polymer electrolyte membrane fuel cell. Three different types of single cells with the electrodes containing (PdPt/C: Pt/C), (Pt/C: PdPt/C) and (PdPt/C: PdPt/C) as their anode and cathode electrocatalysts were fabricated and the performance of them were compared [26,27]. Recent reports on Pd-based catalysts show that Pt can be replaced by these catalysts [28–33]. Hence in this study, the theoretical evaluation of three palladium-based electrocatalysts, Pd₇₀CO₂₀X₁₀ (X = Ni or Mo or Au), paying main attention to changes in their chemisorption energy has been reported.

Advance in computational sciences provides us the opportunity to implement codes and algorithms in which quantum mechanical theories can be applied to predict the behavior of molecular systems. These state-of-the-art codes have been satisfactorily used in many areas of the physical/chemical sciences. The electronic, optical, and structural properties can be simulated using first-principles calculations. Density functional theory (DFT) under the Cambridge Serial Total Energy Package (CASTEP) code has been used to perform these calculations. Besides the structural information, the use of molecular simulation methods allows to understand (a) how the clusters are formed, (b) which atomistic distribution produces the minimum energy configurations, and (c) the most probable configuration in the real material. Poisoning of catalysts by CO molecules is of high importance due to the catalyst deactivation process. Therefore, CO adsorption over the modeled structure is also performed.

2. THEORETICAL CALCULATIONS

Using a CASTEP module, an atomistic model accomplishing both the stoichiometry and XRD pattern was developed for each of the Pd₇₀CO₂₀X₁₀ alloys and pure Pt. For comparison, experimental XRD patterns for Pd-Co-Au and Pd-Co-Mo were taken from references [34] and [35], the pattern and lattice parameter for Pt were taken from the references [36] and [37], Scherrer's formula was considered to calculate the lattice parameter and build up the atomistic model. To assure the correct description of the structure, a simulation of XRD pattern was performed. According to the experimental details [38,39], the simulated diffractometer was set to X-ray, Cu K_α source, with a wavelength of 1.54 Angstrom. Temperature of reaction was determined to be at room temperature (20°C), and CO coverage considered for the calculations was 1 ML.

3. RESULTS AND DISCUSSION

Comparison between literature [34,35,40,41] and calculated XRD patterns for Pt, Pd-Co-Au (70:20:10 atom %) and Pd-Co-Mo (70:20:10 atom %) catalysts for ORR gives a good match between proposed atomistic models and experimental XRD patterns. Figure 1(a, b), which correspond to the comparison of theoretical (calculated) and experimental XRD pattern of Pd-Co-Mo and Pd-Co-Au, respectively. The diffraction peaks are characteristic of a face-centered cubic lattice, but the reflections are shifted to higher angles compared to that of Pd metal, indicating a contraction of the lattice due to alloy formation. It is interesting to note that the samples of Pd-Co-Mo treated at 500°C and Pd-Co-Au treated at 750°C show different specific activity for ORR than the commercial Pt [39]. The specific activity decreases with increasing heat treatment temperature due to an increase in crystallite size and a consequent decrease in surface area.

For the host-solute systems investigated, viz., Ni-Au, Co-Pd, and Co-Pt, it was shown that a strong surface segregation of Au, Pd, and Pt in these alloys can be expected based on DFT calculations, [36] and experimental results [37]. As there is no experimental XRD pattern for Pd-Co-Ni alloy until the writing of this report, it was estimated to be correct and shown in Figure 1(c). Although the experimental and calculated XRD patterns seem to match, an additional step of geometry optimization for each of the tertiary alloy crystals, to approach the minimum energy configuration has been carried out to keep the structure within a reasonable confidence level. This was achieved by using a GGA-RPBE functional with ultrasoft pseudopotentials and a density-mixing scheme for the electronic minimizer. After calculating the optimized structures, (1 1 0) plane has been constructed from the original crystals and their energies were

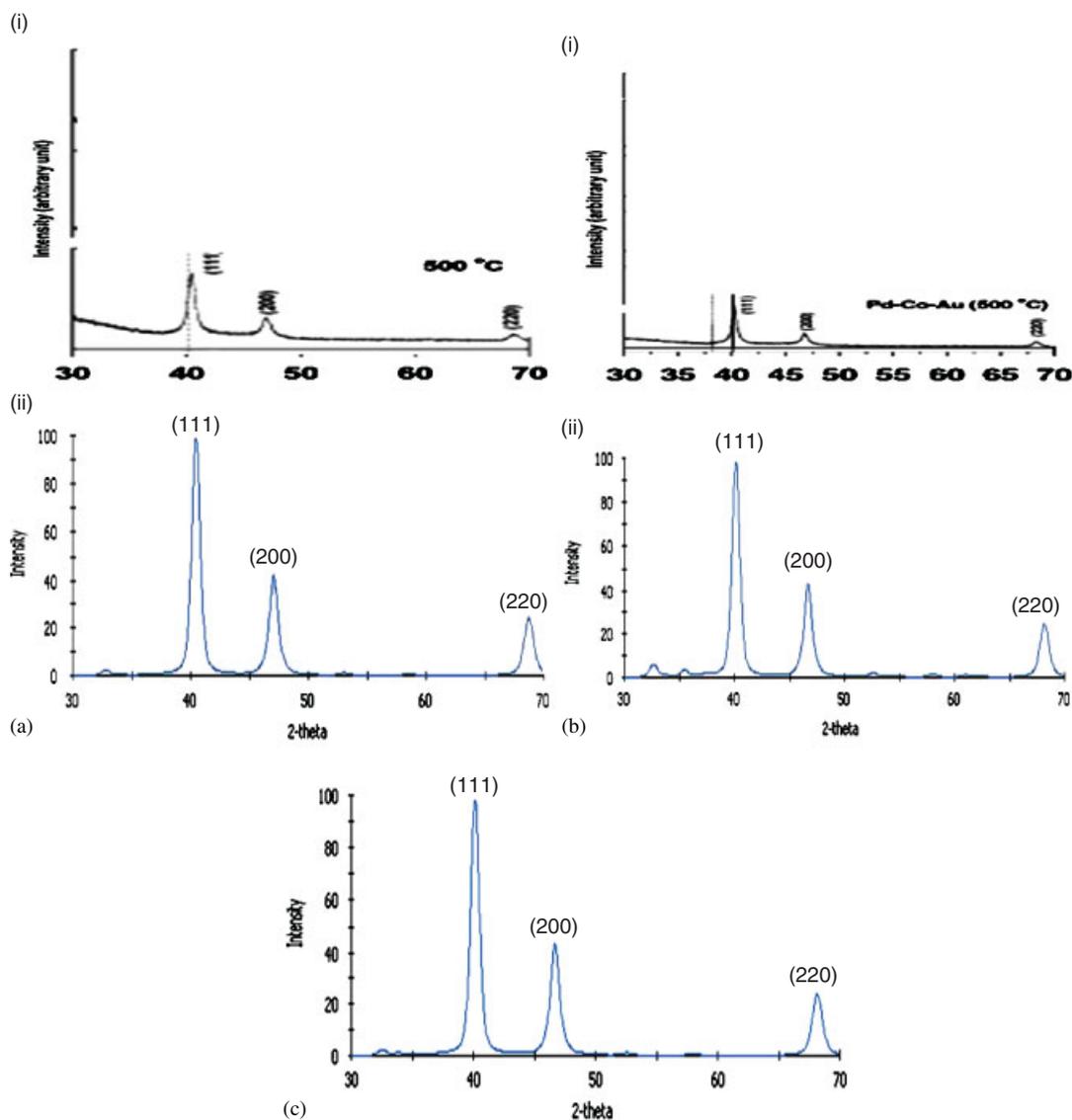


Figure 1. (a). XRD pattern of Pd₇₀Co₂₀Mo₁₀: (i) literature³⁵ (ii) calculated. (b) XRD pattern of Pd₇₀Co₂₀Au₁₀: (i) literature³⁴ (ii) calculated. (c) Simulated XRD pattern for Pd-Co-Ni (70:20:10 atom %) tertiary alloy.

calculated through a geometry optimization process with the same parameters and potentials. Vacuum slab technique was chosen due to its reliability to reproduce experimental chemisorption energies. In parallel, a crystal was built incorporating the poisoning species (CO) and its energy was also calculated. Afterwards, assuming that there is a short-bridge adsorption process of CO by the metallic species, a crystal simulating the CO adsorbed by the alloys was built. A supercell or superlattice is created, as shown in Figures 2–5, and CO molecules were tilted with respect to each other to prevent the self-repulsive forces. Energy was evaluated for all configurations and the chemisorption energies were also estimated.

Chemisorption energies calculated considering room temperature and atmospheric pressure for all the tertiary

composites is shown in Table I. CASTEP calculations were carried out using the general gradient approach—RPBE functional with ultrasoft pseudopotentials. A geometry optimization was developed to run the calculations with the use of a BFGS minimizer. Number of SCF cycles was limited to 500, binding energies of contaminant specie, as well as energies of surface and contaminant specie adsorbed in the short-bridge way to crystal atoms were then calculated. The change in the chemisorption energy for each of the crystals was found using the well-known formula given by

$$\Delta E_{\text{chemisorption}} = 1/2 E_{\text{CO on supercell (110)}} - E_{\text{surface(110)}} - E_{\text{CO}} \quad (1)$$

Where $E_{\text{CO on supercell (110)}}$ is the energy of CO molecule adsorbed by the metallic surface represented

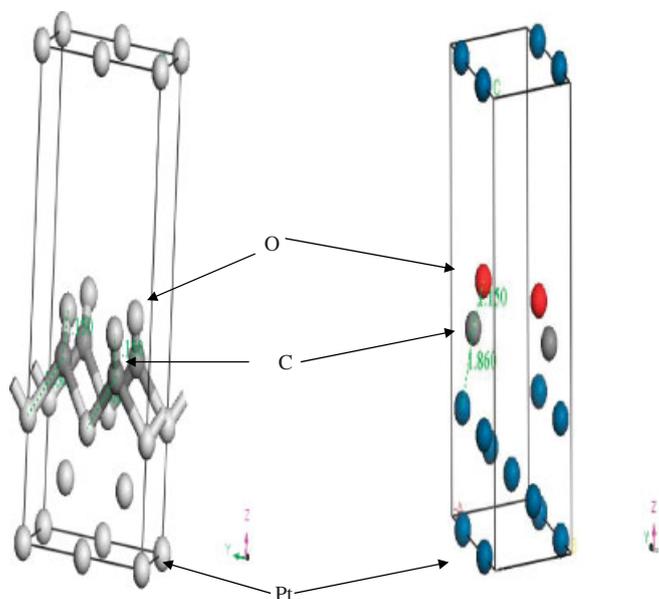


Figure 2. Supercell for the adsorbed CO species on the Pt (1 1 0) plane.

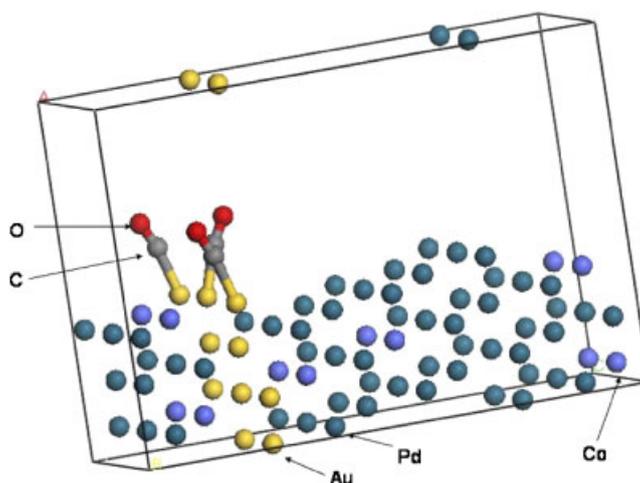


Figure 3. Supercell for the adsorbed CO species on the Pd-Co-Au (1 1 0) plane.

as a supercell, $E_{\text{surface (1 1 0)}}$ is the energy for metallic (1 1 0) surface without the adsorbed specie and E_{CO} is the energy calculated for CO molecule crystal. As seen from Table I, the Pd-Co-Mo tertiary alloy catalyst with a composition of around Pd:Co:Mo = 70:20:10 exhibits high catalytic activity for ORR in PEMFC with good chemical stability and the most CO-tolerant of the three tertiary alloys is Pd-Co-Mo alloy.

4. CONCLUSION

This study demonstrates the feasibility of developing non-platinum alloy compositions that offer catalytic

activity similar to that of platinum. Comparison of the electrochemical properties of these new non-Pt alloy catalysts with that of Pt may also help to develop a better understanding of the mechanisms involved in chemisorption energy. Higher change in the chemisorption energy represents lower probability of the CO to be adsorbed by the crystal. In terms of the Fermi energy, the higher occupancy of the 'd' band near the Fermi level by the electrons of Pt, Pd-Co-Au, and Pd-Co-Ni makes them more susceptible of being attacked by the CO specie, whereas for Pd-Co-Mo crystal, lower occupancy of the 'd' band near the Fermi level yields to less susceptibility of being attacked by the CO specie. Furthermore, we have shown that Pd-Co-Mo tertiary alloy catalyst, with a composition

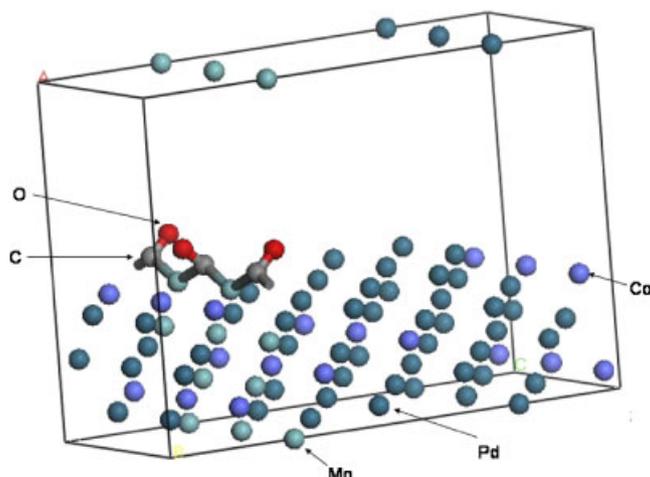


Figure 4. Supercell for the adsorbed CO species on the Pd-Co-Mo (1 1 0) plane.

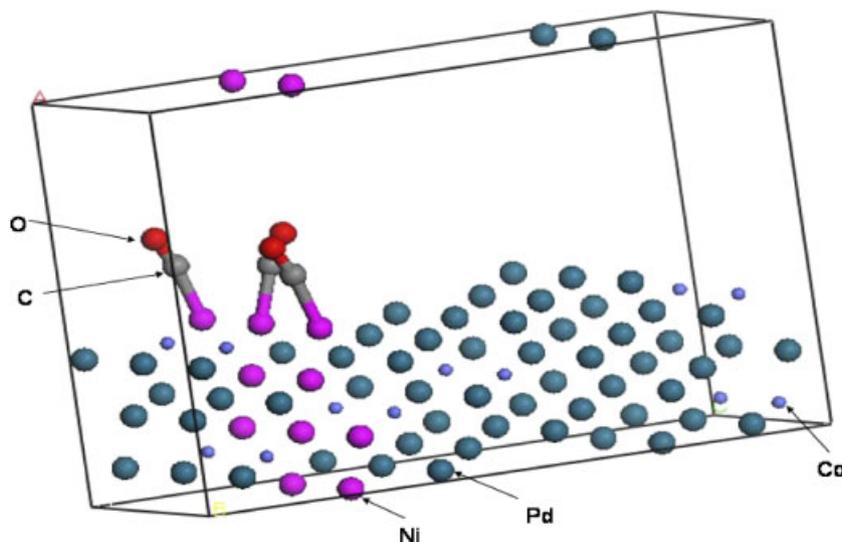


Figure 5. Supercell for the adsorbed CO species on the Pd-Co-Ni (1 1 0) plane.

Table I. Change in chemisorption energies.

Catalyst	Change in chemisorption energy (eV)
Pt	-1.847 [24]
Pd-Co-Au	-587
Pd-Co-Mo	321.9
Pd-Co-Ni	-596.52

of around Pd:Co:Mo = 70.20:10, exhibits high catalytic activity in PEMFC with good chemical stability; and the most CO-tolerant of the three alloys is Pd-Co-Mo alloy. Significantly, lower cost of Pd-Co-Mo, Pd-Co-Au, and Pd-Co-Ni catalysts and the relative abundance of these metals compared with that of Pt could enhance the commercial viability of fuel cell technology. This study demonstrates the feasibility of designing new less

expensive, more efficient non-platinum catalysts for PEMFC and DMFC, enhancing the commercialization prospects of fuel cell technology.

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REFERENCES

1. Paulus UA, Wokaun A, Scherer GG, Schmidt TJ, Stamenkovic V, Markovic NM, Ross PN. Oxygen reduction on high surface area pt-based alloy catalysts in comparison to well defined smooth bulk alloy electrodes. *Journal of Electrochimica Acta* 2002; **47**:3787–3798.
2. Xiong L, Manthiram A. Influence of atomic ordering on the electrocatalytic activity of Pt–Co alloys in alkaline electrolyte and proton exchange membrane fuel cells. *Journal of Material Chemistry* 2004; **14**:1454–1460.
3. Xiong L, Manthiram A. Effect of atomic ordering on the catalytic activity of carbon supported PtM (M = Fe, Co, Ni, and Cu) alloys for oxygen reduction in PEMFCs. *Journal of Electrochemical Society* 2005; **152**(4):A697–A703.
4. Kreidler E, Minor L, Xiong L, He T. Combinatorial discovery of alloy electrocatalysts for oxygen reduction reaction. *Electrocatalysis*, vol. PV11, Brisard G, Adzic R, Birss V, Wieckowski A (eds.). The Electrochemical Society: Pennington, NJ, 2005; 222–230.
5. Luo J, Kariuki N, Han L, Wang L, Zhong CJ, He T. Preparation and characterization of carbon-supported PtVFe electrocatalysts. *Journal of Electrochimica Acta* 2006; **51**:4821–4827.
6. Joo SH, Choi SJ, Oh M, Kwak J, Liu Z, Terasaki O, Ryoo R. Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles. *Nature* 2001; **412**:169.
7. Raghuvver V, Manthiram A. Mesoporous carbon with larger pore diameter as an electrocatalyst support for methanol oxidation. *Journal of Electrochemical and Solid State Letters* 2004; **7**:A336–A339.
8. Toda T, Igarashi H, Uchida H, Watanabe M. Enhancement of the electroreduction of oxygen on Pt alloys with Fe, Ni, and Co. *Journal of Electrochemical Society* 1999; **146**:3750–3756.
9. Toda T, Igarashi H, Watanabe M. Enhancement of the electrocatalytic O₂ reduction on Pt–Fe alloys. *Journal of Electroanalytical Chemistry* 1999; **460**: 258–262.
10. Ralph TR, Hogarth MP. Catalysis for low temperature fuel cells. *Platinum Metals Review* 2002; **46**:3–14.
11. Xie J, Wood III DL, Wayne DM, Zawodzinski TA, Atanassov P, Borup RL. Durability of PEFCs at high humidity conditions. *Journal of Electrochemical Society* 2005; **152**(1):A104–A113.
12. Ye S, Vijn AK. Non-noble metal-carbonized aerogel composites as electrocatalysts for the oxygen reduction reaction. *Electrochemistry Communications* 2003; **5**:272–275.
13. Savadago O, Lee K, Oishi K, Mitsushima S, Kamiya N, Ota KI. New palladium alloys catalyst for the oxygen reduction reaction in an acid medium. *Journal of Electrochemical Communication* 2004; **105**:6.
14. Zen JM, Wang CB. Oxygen reduction on ruthenium oxide pyrochlore produced in a proton exchange membrane. *Journal of Electrochemical Society* 1994; **141**:L51–L52.
15. Raghuvver V, Viswanathan B. Nanocrystalline pyrochlore bonded to proton exchange membrane electrolyte as electrode material for oxygen reduction. *Journal of Material Science* 2005; 6249–6255.
16. Cote R, Lalande G, Faubert G, Guay D, Dodelet JP, Denes G. Non-noble metal-based catalysts for the reduction of oxygen in polymer electrolyte fuel cells. *Journal of New Material Electrochemical Systems* 1998; **1**:7–16.
17. Vante NA, Tributsch H. Energy conversion catalysis using semiconducting transition metal cluster compounds. *Nature* 1986; **323**:431–432.
18. Mano N, Fernandez JL, Kim Y, Shin W, Bard AJ, Heller A. Oxygen is electroreduced to water on a ‘wired’ enzyme electrode at a lesser verpotential than on platinum. *Journal of American Chemical Society* 2003; **125**(50):15290–15291.
19. Mano N, Kim HH, Zhang Y, Heller A. An oxygen cathode operating in a physiological solution. *Journal of American Chemical Society* 2002; **124**(22): 6480–6486.
20. Sawai K, Suzuki N. Heat-treated transition metal hexacyanometallates as electrocatalysts for oxygen reduction insensitive to methanol. *Journal of Electrochemical Society* 2004; **151**:A682–A688.
21. Collman JP, Deniesevich P, Konai Y, Marrocco M, Koval C, Anson FC. Electrode catalysis of the four-electron reduction of oxygen to water by dicobalt face-to-face porphyrins. *Journal of American Chemical Society* 1980; **102**:6027–6036.
22. Gasteiger H, Markovic NM, Ross PN. Electrooxidation of CO and H₂/CO mixtures on a well-characterized Pt₃Sn electrode surface. *Journal of Physical Chemistry* 1995; **99**:8945–8949.
23. Rholand B, Plzak V. The PEMFC-integrated CO oxidation—a novel method of simplifying the fuel cell plant. *Journal of Power Sources* 1999; **84**(2): 183–186.
24. Gouerec P, Denis MC, Guay D, Dodelet JP, Schulz R. High energy ballmilled pt-mo catalysts for polymer electrolyte fuel cells and their tolerance to CO. *Journal of Electrochemical Society* 2000; **147**:3989–3996.
25. Schmidt TJ, Jusys Z, Gasteiger HA, Behm RJ, Endruschat U, Boennemann H. On the CO

- tolerance of novel colloidal PdAu/carbon electrocatalysts. *Journal of Electroanalytical Chemistry* 2001; **501**:132–140.
26. Cho Y-H, Choi B, Cho Y-H, Park H-S, Sung Y-E. Pd-based PdPt(19:1)/C electrocatalyst as an electrode in PEM fuel cell. *Electrochemistry Communications* 2007; **9**:378–381.
27. Antolini E, Salgado JRC, Gonzalez ER. The stability of Pt–M (M = first row transition metal) alloy catalysts and its effect on the activity in low temperature fuel cells: a literature review and tests on a Pt–Co catalyst. *Journal of Power Sources* 2006; **160**:957–968.
28. Pascual JJ, Collins-Martinez V, Lopez Ortiz A, Solorza-Feria o. Low Pt content on the Pd₄₅Pt₅Sn₅₀ cathode catalysts for PEM fuel cell, Salvador. *Journal of Power Sources* 2010; **195**(11):3374.
29. Antolini E, Gonzalez ER. Alkaline direct alcohol fuel cells. *Journal of Power Sources* 2010; **195**:3431.
30. Wang NTS, Liu X, Wang X. Novel Palladium-Lead (Pd-Pb/C) bimetallic catalysts for electrooxidation of ethanol in alkaline media. *Journal of Power Sources* 2010; **195**:2619.
31. Haan JL, Stafford KM, Morgan RD, Masel RI. Performance of the direct formic acid fuel cell with electrochemically modified palladium antimony anode catalyst. *Electrochimica Acta* 2010; **55**:2477.
32. Di Noto V, Synthesis NE. Characterization and electrochemical performance of tri-metal Pt free carbon nitride electrocatalysts for the oxygen reduction reaction. *Electrochimica Acta* 2010; **55**:1407.
33. Miao F, Tao B, Sun L, Liu T, You J, Wang L, Chu PK. Preparation and characterization of novel nickel-palladium electrodes supported by silicon microchannel plates for direct methanol fuel cells. *Journal of Power Sources* 2010; **195**:146.
34. Kittel C. *Introduction to Solid States Physics* (7th edn). Wiley: New York, 2002; 22–23.
35. Zhang X, Chan K. Microemulsion synthesis and electrocatalytic properties of platinum–cobalt nanoparticle. *Journal of Materials Chemistry* 2002; **12**:1203–1206.
36. Christoffersen E, Liu P, Ruban A, Skiver HL, Norskov JK. Anode materials for low temperature fuel cells. *Journal of Catalysis* 2001; **199**:123.
37. Bardi U. The atomic structure of alloy surfaces and surface alloys. *Reports on Progress in Physics* 1994; **57**:939–987.
38. Fernández JL, Raghuvver V, Manthiram A, Bard AJ. Pd–Ti and Pd–Co–Au electrocatalysts as a replacement for platinum for oxygen reduction in proton exchange membrane fuel cells. *Journal of the American Chemical Society* 2005; **127**:13100–13101.
39. Raghuvver V, Manthiram A, Bard AJ. Pd–Co–Mo Electro-catalyst for the oxygen reduction reaction in proton exchange membrane fuel cells. *Journal of Physical Chemistry B* 2005; **109**:22909–22912.
40. Sluiter MHF, Colinet C, Pasturel A. Ab initio calculation of the phase stability in Au-Pd and Ag-Pt alloys. *Physical Review B* 2006; **73**:174–204.
41. Tarasov KA, Isupov VP, Bokhonov BB, Gaponov YA, Tolochko BP, Sharafutdinov MR, Shatskaya SS. Formation of nanosized metal particles of cobalt, nickel, and copper in the matrix of layered double hydroxide. *Journal of Materials Synthesis and Processing* 2000; **8**(1):21–27.